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Geothermometry at the Balmat No. 2 mine, New York by the FeS-ZnS system

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GEOTHERMOMETRY AT THE BALMAT NO. 2 MINE, NEW YORK BY THE FeS-ZnS SYSTEM

BY

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A

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I. INTRODUCTION

Definition Of The Study The study consists of an investigation of the variation in the temperature of formation of sphalerite on the 500 and 1500 ft levels of the Balmat zinc deposit at Balmat, New York. A subsidiary investigation was performed on the use of x-ray fluorescence as a means of chemical quantitative analysis. Twelve samples of sphalerite from the 500 ft level and 13 samples from the 1500 ft level were analyzed for atomic percent iron content by measuring Zn/Fe x-ray fluorescent ratios. The x-ray fluorescent ratios were standardized by "wet" quantitative analysis. The results of the analyses are applied to the FeS-ZnS phase diagram developed by Kullerud (1953). The locations of the samples from Balmat are recorded on maps of the two levels to enable a study of the horizontal and vertical variation of the temperature of formation.

Reason For The Study This study was undertaken to determine the physical conditions of the ore forming fluid which originated the Balmat deposit. It is hoped that the results of this study may guide similar studies in other areas. In addition to the above, the study was initiated to shed some light on the following questions:

1. The direction of approach of the ore fluids.
2. The relationship of different stopes of ore to each other.
3. How the sphalerite ore may be zoned with respect to temperature of formation.

The factors controlling the localization of mineral deposits are not readily apparent because of an incomplete understanding of the interaction of a number of variables. A list of the principle variables influencing ore deposition is:

1. The chemical nature of the ore bearing fluid.

2. The chemical effect of the wall rock on the ore bearing fluid.

3. The temperature of formation at the time of ore deposition.

4. The pressure of formation at the time of ore deposition.

Two more factors of importance, but considered to be subsidiary to the previous four, are the origin of the ore fluid and the path of movement of the ore fluid.

Little direct evidence is available on the nature of sulfide bearing ore fluids. Liquid inclusions and thermal spring deposits furnish all the direct evidence on ore carrying fluids known to the author. In order to obtain a thorough understanding of the ore fluid it will be necessary to first solve for the wall rock effect, and the temperature and pressure of formation. A knowledge of the temperature of formation of a deposit might place some immediate limits on an ore fluid. The following example is given to illustrate some of the effects a study of the temperature at deposition might have.

The geology of Balmat, New York, the area chosen for study, has been basically described by Brown (1936a, 1936b, 1947). Brown (1947; p. 536) found that the pore openings in the wall rock at the Edwards and Balmat deposits are of capillary size, and there are no openings of visible size with any continuity. In trying to determine an ore medium that might be able to penetrate the rocks, Brown (1947; p. 539) postulated a metallic vapor coupled with water vapor. A temperature study might indicate the state of the water present. Ingerson (1947; p. 379) states that while the critical temperature of pure water is 374°C a solution of 10 weight percent NaCl or KCl increases the critical temperature of the solution 63°C. Ten weight percent was chosen because available data indicates salinity of quartz

inclusions to be of that order of magnitude (Ingerson, 1947; p. 378). Kullerud's study (1953) of the system FeS-ZnS provides a new satisfactory geologic thermometer for use in sphalerite deposits. Utilizing the FeS-ZnS system, a better estimate may be made of the state of the water present at the time of ore deposition.

It seems improbable that ore is deposited in the direction of increasing temperature. A pattern of variation in temperature of formation may delineate the direction of flow of the ore fluid.

The aid that knowledge of the temperature of formation may prove to mining operations warrants further investigation. An ore deposit may be zoned on the basis of temperature of formation isotherms. A uniform temperature of formation may indicate a uniform composition of the ore. A new aid to ore development is indicated.

Acknowledgments The author expresses his appreciation to Prof. Phillip M. Bethke who acted as adviser on the thesis and also supervised the x-ray fluorescence work. Dr. John S. Brown, Dr. Severn Brown, and the St. Joseph Lead Company supplied the samples, photostats, and greatly aided in relating the experimental results to geology. Prof. M. E. Straumanis aided on the fluorescent work and on the quantitative x-ray parameter measurement method. Prof. W. H. Webb recommended the "wet" quantitative procedure. Professors O. R. Grawe, M. P. Nackowski, R. O. Sutherland and Adolph Legsdin aided on various parts of the study. Mr. Herb Pruett machined the sample holders for the fluorescent analysis.

II. PREVIOUS WORK

An excellent review of the methods and problems of geothermometry is presented by Ingerson (1956; p. 341-410). It is unnecessary to give a comprehensive survey of current methods employed in geothermometry. The FeS-ZnS system and the liquid inclusion method are important to the study and will be explained more fully.

The FeS-ZnS System The FeS-ZnS system was worked out by Kullerud (1953). The amount of iron that will enter the sphalerite structure is proportional to the temperature of formation. Because the introduction of iron causes an expansion of the lattice, the amount of iron that will enter sphalerite is proportional to the pressure also. Kullerud (1953; p. 106) calculated the effect of pressure. It was found that for a given content of FeS an increase in the pressure of formation of 1000 atm would necessitate an increase of approximately 25°C. to maintain equilibrium (Kullerud, 1953; p. 127). Kullerud (1953; p. 138) found the temperature of formation of a sphalerite sample of 8.3 weight percent FeS at Balmat to be 325 $\pm$ 25°C if the pressure of formation is 2000 $\pm$ 1000 atm.

Several assumptions are made in using the FeS-ZnS geothermometer. A list of the assumptions is:

1. LeChatelier's Principle does not apply. Upon the addition of an excess of iron a reaction must not take place which will use up some of the excess beyond equilibrium conditions.
2. Enough iron is present to meet equilibrium conditions.
3. Equilibrium is established between iron and sphalerite at the time of deposition.
4. No iron or zinc is added or subtracted after crystal formation.
5. There are no fluxes present that effect the equilibrium.

6. The presence of foreign cations does not effect the FeS-ZnS equilibrium.

7. The presence of excess sulfur or other anions does not effect the FeS-ZnS equilibrium.

8. Pyrite-sphalerite equilibrium is not appreciably different from pyrrhotite-sphalerite equilibrium.

9. There are no iron or zinc bearing inclusions to give a false estimate of the Zn/Fe ratios.

10. An estimate of the pressure can be calculated.

Most of the assumptions mentioned above seem to be reasonable. LeChatelier's Principle does not seem to apply. Kullerud (1953; p. 80) found that the maximum amount of iron that sphalerite will hold at 894°C is 36.5 wt percent FeS although bombs were made with 50 wt percent and 40 wt percent FeS.

Kullerud tested the effects of foreign cations by mixing cadmium and manganese sulfides with pure ZnS. Both cadmium and manganese enter the sphalerite lattice. Both cadmium and manganese expand the ZnS lattice (Kullerud, 1953; p. 114,116). The expansion effect of Fe, Cd and Mn is additive, and the amount of iron that will fit into the sphalerite lattice is neither increased or decreased by the presence of manganese or cadmium in small amounts (Kullerud, 1953; p. 118). Kullerud states (1953; p. 119), "From the above observations, it may be concluded that at least fairly small amounts of MnS and CdS will have no, or at least very little, influence on the solubility of FeS in 'beta' ZnS." The assumption that the common cations will not effect the FeS-ZnS equilibrium is at least supported by Kullerud's Fe, Cd, and Mn experiments.

A number of fluxes were mixed in with the sulfides to speed up the reaction rate on runs below 750°C. Kullerud found that the presence of any

of the fluxes greatly influenced the FeS-ZnS equilibrium (1953; p. 100). In fact a certain un-named flux was found to completely expel the FeS from the ZnS lattice (Kullerud, 1953; p. 100). The effect of fluxes on the FeS-ZnS equilibrium remains a definite possible source for the introduction of error in temperature calculations.

The activity of FeS in pyrite is less than five percent smaller than that of stoichiometric FeS (Kullerud, 1953; p. 108). Thus it is found that the solubility of FeS in ZnS is decreased by two percent when pyrite forms the system with sphalerite (1953; p. 109). When the amount of 'elemental' sulfur present exceeds the amount that can be accounted for by equating the FeS to pyrite, the activity of the FeS is sharply decreased, and Fig. 1 may not be used as a geologic thermometer (1953; p. 109). Kullerud tested the formation of (Fe,Zn)S from a Fe-Zn alloy by passing a 1:1 mixture of H_2S/H_2 over the alloy at temperatures around 400°C (1953; p. 99). The latter method was used to find the FeS-ZnS equilibrium at 400°C. No radical change in the curve is noticed so that it may be assumed with some degree of confidence that H_2S will not effect the FeS-ZnS equilibrium. Since H_2S is very likely present in ore fluids, this is an important assumption.

If inseparable iron or zinc bearing inclusions are present in the sphalerite, the sample is not usable. It may be that small inclusions oriented in the sphalerite are pyrrhotite that have exsolved from the ZnS lattice over geologic time to come into equilibrium with present pressure-temperature conditions. The latter inclusions are important in calculating the true temperature of formation. Inclusions that do not contain iron or zinc may be discounted by measuring Zn/Fe ratios. The more accurately the

pressure of formation is known, the more accurately the temperature of formation may be calculated. Fig. 4 shows the effect of pressure on the FeS-ZnS temperature-composition diagram.

The reaction rate between FeS and ZnS is extremely slow below 400°C. Below 400°C, the phase diagram is based upon empirical values fitted into a free energy equation (For derivation see Kullerud, 1953; p. 100-104):

$$T \cdot \ln(\ln x) = \text{Constant}$$

The latter equation yields a straight line when plotted on log paper. The curve defined by the latter equation from the empirical results at higher temperatures is extrapolated to 138°C. Since pyrrhotite inverts at about 138°C from the NiAs structure to a 'supercell' with an unknown heat of formation, Kullerud was unable to continue the phase diagram below 138°C (1953; p. 104). The solution of the FeS-ZnS system below 138°C would be extremely valuable since most Mississippi Valley lead-zinc deposits probably formed below 138°C. Kullerud ran one test on Joplin deposits with results indicating the temperature of formation of the ZnS less than 138°.

From the discussion given above, it will be seen that the following assumptions must hold true for correct use of the FeS-ZnS geothermometer:

1. Equilibrium is established between FeS and ZnS.
2. Enough iron is present to satisfy equilibrium conditions.
3. No iron or zinc is subtracted or added after crystalization.
4. The effect of any fluxes that may be present is negligible.
5. The effect of any inclusions that may be present are either insignificant or can be discounted by measuring Zn/Fe ratios.
6. The amount of free sulfur available for reaction does not exceed the amount that can be accounted for by FeS_2.
7. For an accuracy of ± 25°C, the pressure of formation must be known within ± 1000 atm.

The equilibrium diagram for the sphalerite-pyrrhotite system is given in Fig. 1. The data from which Fig. 1 is drawn is given in Table 1. Columns 1-3 of Table 1 are taken from a personal communication with Gunnar Kullerud. The other five columns of Table 1 are derived from the first three. The latter five columns are used later in this paper to standardize working curves for determining atomic percent iron in sphalerite.

Table 1: A Summary of Data Used For Working Curves

Temp °C	Wt % FeS	Mol. % FeS	Wt % ZnS	Wt % Fe	Wt % Zn	Wt % Zn / Wt % Fe	Atomic % Fe
894	36.5	38.9	63.5	23.2	42.6	1.84	24.7
850	33.0	35.3	67.0	21.0	45.0	2.14	22.4
800	29.8	32.0	70.2	18.9	47.1	2.49	20.3
750	26.7	28.7	73.3	17.0	49.2	2.90	18.2
700	24.0	25.9	76.0	15.2	51.0	3.34	16.4
600	19.0	20.6	81.0	12.1	54.4	4.50	13.1
500	14.7	16.0	85.3	9.34	57.2	6.13	10.2
400	11.0	12.0	89.0	6.99	59.7	8.54	7.62
300	7.45	8.19	92.55	4.73	62.1	13.1	5.20
200	4.80	5.29	95.20	3.05	63.9	20.9	3.36
138	4.00	4.41	96.00	2.54	64.4	25.4	2.80

Kullerud calculated the values of the molecular percents of FeS from the weight percents by use of the formula:

$$A = \frac{110.85\,(a)}{0.1085(a) + 100}$$

A is mol. % FeS
a is wt % FeS

The author checked the formula given above by the following calculation for a sample of 30 wt percent Fe:

$$A = \frac{110.85(30)}{0.1085(30) + 100} = 32.2 \text{ mol. \% FeS} \qquad (1a)$$

$$\frac{\text{wt \% FeS}}{\text{mol. wt FeS}} = \frac{30}{87.91} = 0.342 \qquad (2a)$$

$$\frac{\text{wt \% Zn}}{\text{mol. wt ZnS}} = \frac{70}{97.44} = 0.720 \qquad (2b)$$

$$\text{Mol. propor. FeS + mol. propor. ZnS} = 0.342 + 0.720 = 1.062 \qquad (2c)$$

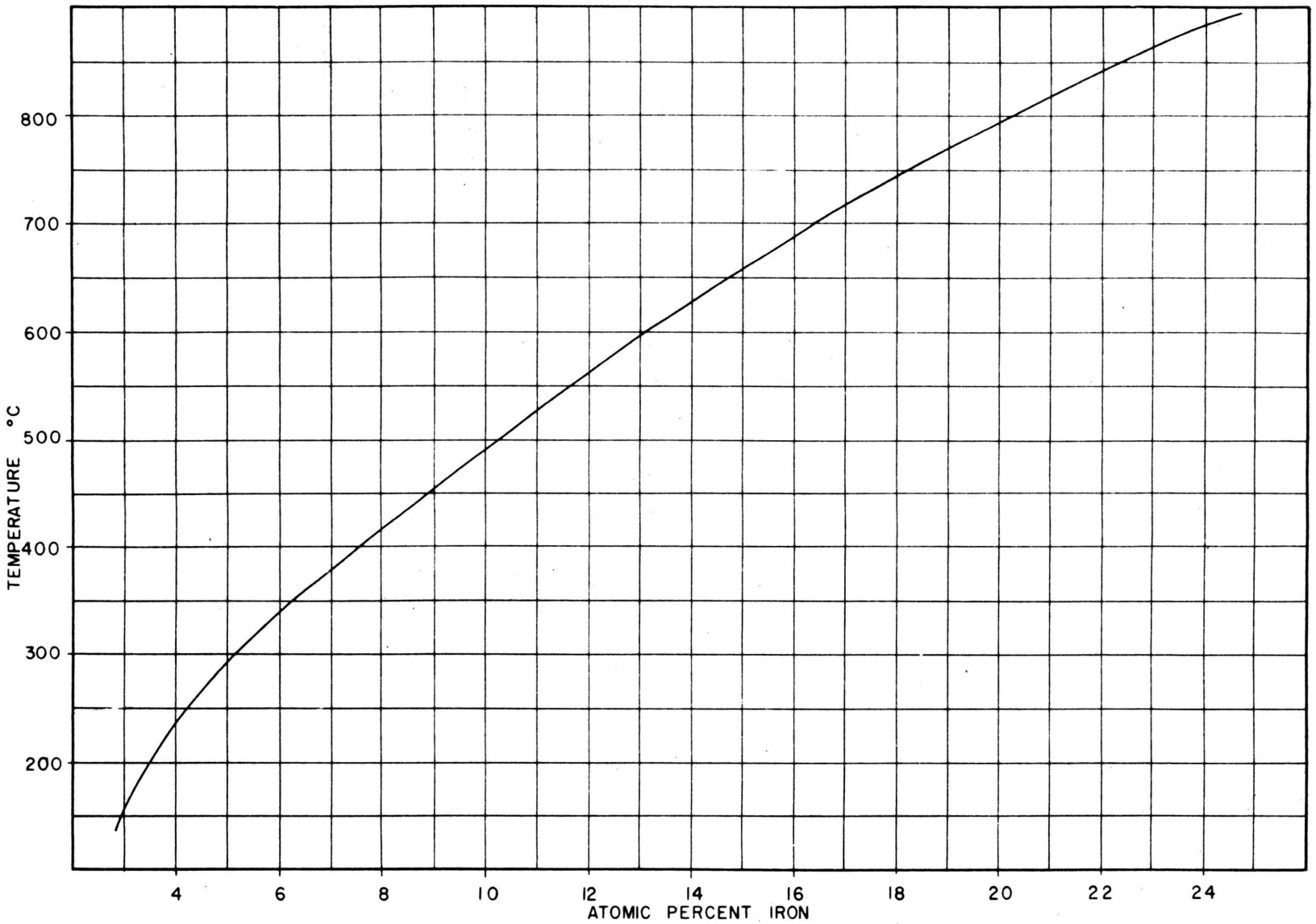


FIG. 1: THE (Fe,Zn)S EQUILIBRIUM DIAGRAM BETWEEN 138°C AND 894°C (1 ATM)

(Calculated From Kullerud Weight Percent Data; 1953, p. 98)

$$\text{Mol. \% FeS} = \frac{0.342\ (100)}{1.062} = 32.2 \qquad (2d)$$

The values for the atomic weights of the elements were taken from a periodic chart compiled by Henry D. Hubbard (1941):

Sulfur	32.06
Iron	55.85
Zinc	65.38

The atomic weights given above give values of:

FeS = 63.53 Atomic % Fe
ZnS = 67.10 Atomic % Zn

Two Phase Fluid Inclusions The most common method of determining geologic temperatures has been to measure the temperature of disappearance of the phase boundary in two phase inclusions in minerals. The temperature of disappearance is usually measured on a thick 'thin section' placed in a heating stage and examined under a petrographic microscope. At elevated temperatures, fluids have a coefficient of expansion which is proportional to the existing temperature and pressure.

If an inclusion of ore fluid is trapped inside a mineral which crystallizes at a given temperature, the fluid will contract when the temperature drops and will expand slightly when the pressure drops. The fluid usually contracts enough so that a liquid phase forms that does not completely fill the cavity at room temperature and therefore will leave a bubble.

The compressibility of crystals is probably negligible, and the cavity may be considered to be a system of defined size. A two phase inclusion at room temperature may indicate the inclusion was formed at some elevated temperature and pressure when only one phase occupied the cavity. If the pressure on the system is raised, the fluid will be compressed, and the degree of filling will decrease. In order to bring the degree of filling

back to the original value under the new pressure, the temperature must increase. Thus many different pressure-temperature combinations will yield a similar degree of filling.

If the fluid started out as one phase, the example given above provides a means of estimating the temperature of formation of the mineral that contains the inclusion if the pressure at the time of formation is known. This is true because the degree of filling at room temperature will be proportional to the temperature and pressure of formation of the inclusion if the inclusion was completely filled with the one phase at the time of deposition. For a given pressure only one temperature exists where the fluid will just fill the cavity. From Fig. 5a may be seen that a pressure increase of 1000 atm raises the equilibrium temperature by approximately 50°C.

Peach, 1951; Bailey, 1949; Scott, 1948; Ingerson, 1947; and Newhouse, 1933 are among those who have performed fluid inclusion studies in geothermometry. Bailey (1949; p. 304) tabulates the assumptions made in using the liquid inclusion method of geothermometry:

1. The liquid completely filled the cavity at the time of crystallization.
2. The liquid is an aqueous solution uniform in concentration from inclusion to inclusion within a single crystal and containing no carbon dioxide.
3. The pressure on the liquid at the time of inclusion can be estimated.
4. Primary liquid inclusions can be distinguished from secondary inclusions.
5. There has been no significant change in the volume of the cavity itself due to pressure, solution, or precipitation.
6. There has been no addition or loss of liquid from the cavity.

7. The samples used are representative of the deposit under study.

8. Secondary inclusions can be distinguished from primary inclusions.

Ingerson notes three difficulties inherent to the method (1947):

1. Observational difficulties in determining exactly when the two phase boundary has disappeared.

2. Inclusion leakage during experimentation.

3. Pressure estimates are extremely difficult.

Kennedy (1950; p. 543-546) points out three significant assumptions:

1. Gas has not leaked out of the vacule over geologic time to come into equilibrium with the surroundings. No leakage occurred along lineage boundaries.

2. No liquid or gas has moved into the cavity.

3. The effects of the constituents of the ore solution are known. For example CO_2 with H_2O would be more compressible than pure water while salts dissolved in water would yield a less compressible solution than pure water.

In applying the fluid inclusion method to sphalerite geothermometry, it should be remembered that sphalerite has excellent cleavage which would give fluids a good chance to leak in or out over geologic time.

The fluid inclusion method used in combination with the ZnS-FeS geothermometer provides a convenient and relatively accurate method of estimating the pressure and temperature of mineral formation. This pressure-temperature gauge will be discussed more fully in Section V.

III. QUANTITATIVE ANALYSIS

Mineral Separation Since pyrite is one of the least magnetic of minerals and sphalerite, especially the marmatite variety, has a rather high magnetic susceptibility, a primary separation of pyrite from sphalerite was performed by use of a Meta-Magnet Associates electromagnet with a maximum of nine amperes passed on a 110 A.C. circuit. Samples 1, 3, and 4 contained magnetite which made the separation on these samples difficult to perform magnetically. Most of the magnetite was removed by passing an alnico magnet over the crushed sample. The rest of the magnetite was removed with a magnetized needle under a 3X binocular microscope.

Much gangue and some pyrite still remained adhered to the sphalerite. Each sample was then hand picked twice at plus forty mesh under a 3X binocular microscope to eliminate as much gangue as possible. Samples 15 and 16 contained hematite, but the separation is judged to be good. In sample 8 the separation of the pyrite from the sphalerite is judged to be good, but it was impossible to get rid of all the gangue. The effect of the gangue should have been discounted by measuring Zn/Fe ratios. Samples 7 and 12 had thin pyrite 'leaves' which were wrapped around the sphalerite making complete separation extremely difficult. The values obtained from samples 7 and 12 are of questionable accuracy.

Sample number 10 is a mixture of dark and light sphalerite. Many individual grains graded from brown to tan. For the latter reasons sample 10 is viewed in a questionable light. In some samples pyrite occurred as cubes and in others as pyritohedrons. In sample number 2 both pyritohedrons and cubes occur. Why pyrite sometimes forms cubes and other times pyritohedrons is not well understood. After the sphalerite was separated

from the hand specimen, the sphalerite was analyzed for Zn/Fe ratios by x-ray fluorescence techniques standardized by 'wet' quantitative analysis. By measuring Zn/Fe ratios, non iron and zinc gangue is discounted in determining atomic percent iron.

The amount of iron in sphalerite can be measured by many means. The higher the iron content, the higher the index of refraction (Winchell, 1951; p. 42). The higher the iron content, the higher the refringence under lithium and sodium light (Winchell, 1951; p. 42). The higher the iron content the lower the specific gravity (Winchell, 1951; p. 42). The higher the iron content, the lower the inversion temperature to wurtzite (Kullerud, 1953; p. 65) (Winchell, 1951; p. 42). The higher the iron content, the larger is the lattice parameter (5.398-5.413) (Kullerud, 1953; p. 77). Probably the iron content is proportional to the magnetic susceptibility also. Pure ZnS is diamagnetic while the (Fe,Zn)S crystals are paramagnetic. The author noticed that upon separating the sphalerite with a magnetic needle some sphalerite could be picked up while other grains could not.

Many of the methods mentioned above are also influenced by other elements (especially cadmium) such as lattice parameters, inversion temperature, and probably the optical methods. It is for the above reasons that the author decided to utilize direct measurements of the iron content.

Volumetric Zinc The volumetric zinc procedure used was basically that given by Koltoff and Sandell (1952; p. 549-551). The method uses a potassium ferrocyanide titration with a diphenylamine internal indicator. The endpoint is passed and brought back with a zinc standard back-titration.

The zinc standard was formed by dissolving 3.1118 gm of ZnO (previously

heated to a dull red for ten minutes) in 500 ml of 1.20 sp gr sulfuric acid. ZnO is 80.34 wt percent Zn. The zinc standard contains 0.005 gm Zn/ ml.

22.0007 gm of potassium ferrocyanide was dissolved in one liter of distilled water. To 20 or 40 ml of zinc oxide standard was added 25 ml of distilled water, 15 ml of 1.20 sp gr sulfuric acid, two grams of ammonium sulfate buffer salt, three drops of one percent potassium ferricyanide solution and three drops of one percent diphenylamine indicator solution. Two milliliters of the ferrocyanide solution were added to the zinc standard before the addition of the ferricyanide and diphenylamine to facilitate the formation of the initial blue color. The zinc standard was further titrated with ferrocyanide until the blue color changed to a cream. The speed of titration was diminished as the end point was approached. An attempt was made not to add more than a milliliter of ferrocyanide in excess. The sample was then back-titrated slowly with zinc standard to the first appearance of the purple color. The results of the standardization of the potassium ferrocyanide are shown in Table 2.

Table 2: Ferrocyanide Standardization

Run	Zn Sol. ml.	Ferrocyanide ml	Back Tit. Zn Sol. ml	Zinc Equivalents mg/ml
1.	20	17.92	0.60	5.748 - 0.012
2.	20	18.08	0.83	5.761 + 0.001
3.	20	17.65	0.27	5.770 + 0.010
			Average	5.760 ± 0.008

It is recommended by Koltoff and Sandell that the same procedure should be used in the analysis of unknowns as is used in standardization.

Volumetric Iron The volumetric iron procedure is a potassium permanganate titration standardized by Mohr's salt (14.13 wt % Fe). The potassium permanganate solution was diluted to twice the original volume because the

size of the samples run was limited and the samples contained a small percentage of iron. 1.4000 gm of Mohr's salt was dissolved in 200 ml of 1.20 sp gr sulfuric acid and titrated immediately with permanganate. The standardization was rerun using 1.3998 gm of Mohr's salt. The results of the permanganate standardization are given in Table 3.

Table 3: Permanganate Standardization

Run	Mohr's salt gm	Fe Content gm	Titration ml	Equivalents mg/ml
1	1.4000	0.1978	79.30	2.494
2	1.3998	0.19779	79.06	2.502
				Average 2.498 ± 0.004

Iron-Zinc Flowsheet Approximately 0.4 gm of sample was weighed out. The sample was treated with 10 ml of concentrated HCl and gently heated. The beaker was covered with a watch glass. After the sample was dissolved, one-half milliliter of 1:4 HNO_3 was added and the resulting solution was boiled until chlorine gas was given off. The cover glass and beaker wall were washed with distilled water. Concentrated ammonium hydroxide was added with an eye dropper in small excess. Five milliliters of bromine water were added and the resulting solution was boiled gently to get rid of the excess bromine.

The precipitates of the iron, aluminum, and manganese hydroxides were filtered off. The precipitate was dissolved in hot 1:4 HCl and precipitated again by addition of ammonium hydroxide and bromine water as before. The precipitate was washed with water containing NH_4OH and NH_4Cl. The filtrates were united.

The zinc (filtrate) was determined in the same manner as in the zinc standardization, except that the solution was boiled with a small amount of

test lead just before titration to get rid of any copper present. The iron precipitate was dissolved in hot dilute HCl, heated gently, covered with a cover glass, and SnCl was added drop by drop until the solution lost its yellow color. The cover glass and sides of the beaker were washed with small amounts of water. The solution was diluted to 500 ml and stirred rapidly while adding 10 ml HgCl and 25 ml of 'preventive solution'. The resulting solution was titrated immediately with the permanganate. The 'preventive solution' contains 90 gm of manganous sulfate in 650 ml of water, to which are added 175 ml of concentrated sulfuric acid and 175 ml of phosphoric acid. The purpose of the 'preventive' solution is to render the chloride present harmless. Otherwise the chloride would interfere with the permanganate titration. A complete data sheet of the analyses is given in Appendix III.

X-Ray Fluorescence A Norelco x-ray spectrograph (Type No. 52157) was attached to a Norelco water cooled x-ray diffraction unit. The sample was bombarded with white tungsten radiation produced at 50 kv and 20 ma.

The geiger tube used in the present research was tested for linearity by plotting the intensity of the x-rays transmitted (counts per second) against successive thicknesses of Ni foil. The results of the geiger tube test are expressed in Fig. 7 in Appendix II. It will be noticed that the plot is a straight line between 30 and 500 counts per second. No intensities were used which fell outside the known linearity range of the geiger tube.

The intensity of the first order zinc K_a line was found to be too great with respect to the iron K_a line to be able to measure both peaks quantitatively on one scaler setting. The second order zinc K_a ($2K_a$) was used which

exercised to obtain reproducible results. It is recommended that constant time and constant count methods of measuring intensity be investiaged to eliminate the planimeter measurements. The time consumed in planimetering a sample was approximately one hour. Approximately 1-3/4 hours were spent in recording the peaks for one sample.

It will be noticed that the low angle side (right) of Fig. 8A has the background grass on a higher level than on the high angle side. In this case the lower background was chosen as the true background, as shown. Fig. 8B shows the erratic type peak that was observed frequently on high zinc peaks and sometimes on iron peaks (see above). Ratios of Zn to Fe from the erratic curves agreed with the ratios of the more conventional peaks. No strong peaks of other elements occur near the $2K_a$ line. A way of loading the sample holder was developed which eliminated the appearance of the erratic peak (see below). A function of sample width may be indicated because a fine powder coating lapped over the side of the well in many cases of sample holder loading by methods other than that described below.

The sample holder was a block of leucite 1-5/16 x 1-15/16 x 3/8 inches. A hole of approximately one centimeter was drilled through the block, and a plug was fashioned that would snuggly fit into the hole making a well. The plug was capable of completely filling the hole. A fluorescence test run was made on the sample holder. No iron or zinc peaks were observed. A nickel peak appeared which may be accounted for by the clip needed to hold the leucite sample holder in place in the fluorescence chamber. Leucite is very transparent to x-rays so that care must be taken in the choice of backing used to keep the sample holder in place. The author built up a

backing of leucite and glass to keep the clip previously mentioned from disturbing the sample holder plug.

The sample holder was loaded by fastening the holder to a glass plate with two pieces of Scotch tape. It is fairly important that the sample holder remain tightly pressed against the glass plate. The sample, which was ground fine enough to pass through Miller's cloth, was poured into the resulting well. The plug was inserted and pressed into place by holding the sample holder and glass plate in the left hand and applying pressure by placing the right fore-finger under the well on the glass plate with the right thumb on the extruding plug. It is necessary for the glass plate to be quite clean or some of the sample will adhere to the plate destroying the smooth surface of the sample.

Leucite is a satisfactory material for a holder, and approximately 50 hours of use may be expected if care is taken. At 50 kv and 20 ma, the author found that the leucite would start to 'boil' if bombarded with x-rays for periods of greater than two or three hours at a time. After several hours of exposure to x-rays, the leucite becomes quite brittle, and care must be taken that no lateral pressures are put on the leucite plug or the block will crack.

It might be mentioned here that, although the Norelco unit on the Missouri School of Mines campus has voltage and amperage compensators that operate up to five percent fluctuation, voltage and current fluctuations are so great during the day that the machine will constantly shut down if operation at 50 kv and 20 ma is desired. During the daytime it is also difficult to maintain water pressure although a water pressure booster is attached to the machine. Saturdays and Sundays are as bad as weekdays.

enabled measurement of the fluorescent Zn/Fe ratios on a scale factor of 8, a multiplier factor of 0.8, and a time constant of 4 seconds. With the above setting, a full scale deflection is 320 counts per second.

The iron K_a peak is at 40.18° 2θ and was scanned between 38° and 42°. The zinc $2K_a$ peak is at 61.24° 2θ and was scanned between 59° and 63°. Most peaks were scanned three times at a rate of 0.25° per minute to test precision. Samples 14, 22, and 24 were each removed, repacked, and reinserted in the machine to test reproducibility (See Appendix I). Reproducibility was found to lie within 0.02 or approximately to plus or minus one percent for the fluorescent Zn/Fe ratios. The summary of the fluorescent Zn/Fe ratios may be observed in the second column of Table 4.

The areas under the Brown recorder curves are proportional to the intensity of fluorescent radiation. Examples of these curves may be observed in Fig. 8 in Appendix II. Two curves are shown in Fig. 8, a normal curve (A) and an abnormal curve (B) which has several peaks. The abnormal curve may be similar to that given by Klug and Alexander (1954; p. 308) characteristic of small time constant and slow scanning speed. The area under these curves was determined by drawing a base line at the bottom of the background 'grass' and then lines from the base line tangent to the lower part of the peak curve as shown in Fig. 8A.

The instrument used to determine the areas under the curves is a Lasico compensating polar planimeter No. 123A which has a precision measure of 0.005 units. Greater accuracy in the third place was attempted by averaging the sum of five accumulative readings. Reproducibility was found to be quite difficult to achieve so that the utmost care must be

Nights are better because the campus switches to city power from campus power.

The x-ray fluorescence procedure was standardized by 'wet' quantitative analysis as described above. Fig. 2 is given to enable conversion from Zn/Fe weight ratios to atomic percent iron in sphalerite (see the last two columns of Table 1). Fig. 3 shows the relationship of fluorescent Zn/Fe ratios and atomic percent iron in sphalerite. Fig. 3 was plotted from the data of those samples on which 'wet' analyses were run (see Table 4).

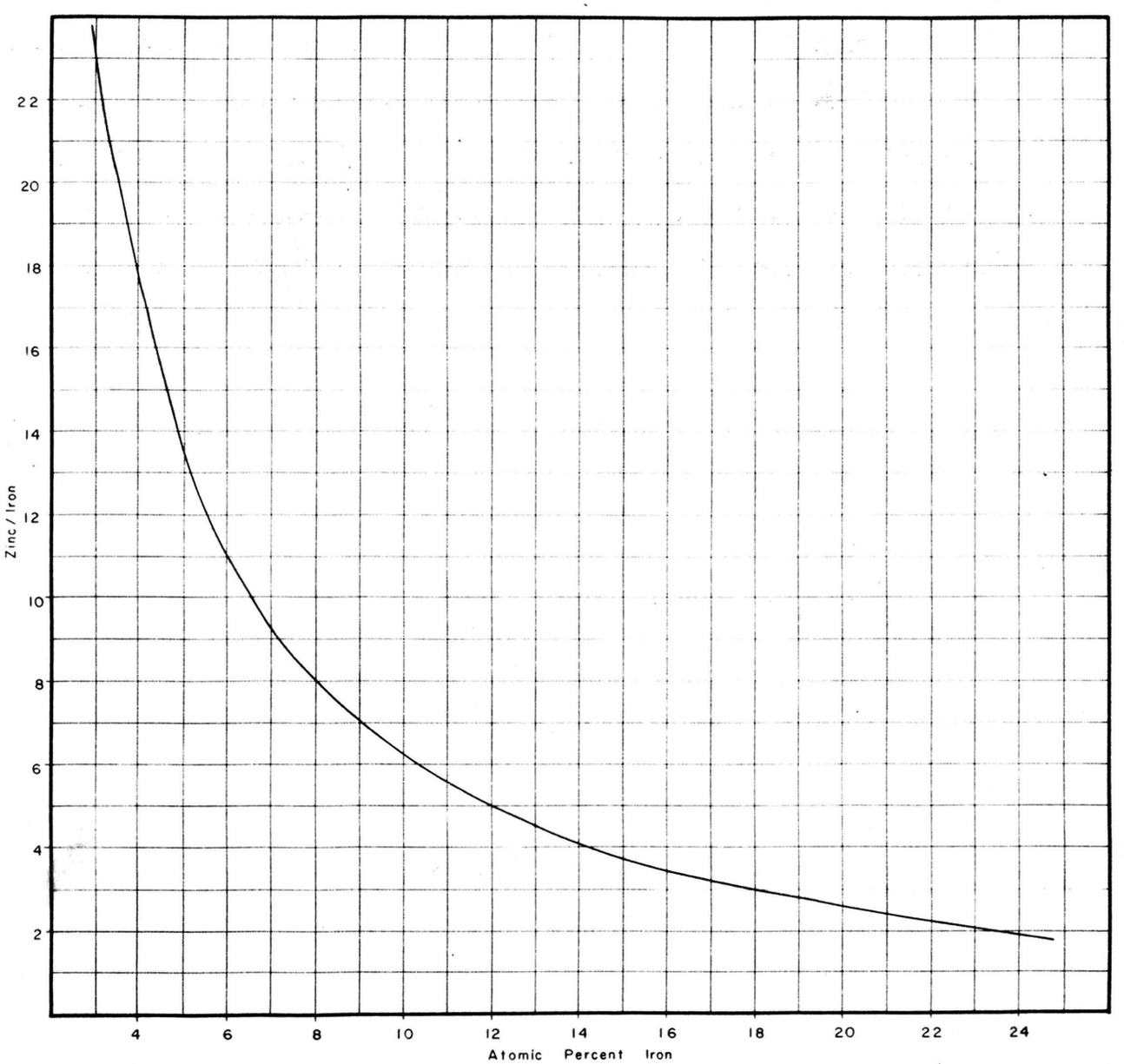


FIG. 2: DIAGRAM TO CONVERT Zn/Fe WEIGHT RATIOS TO ATOMIC PERCENT IRON IN SPHALERITE

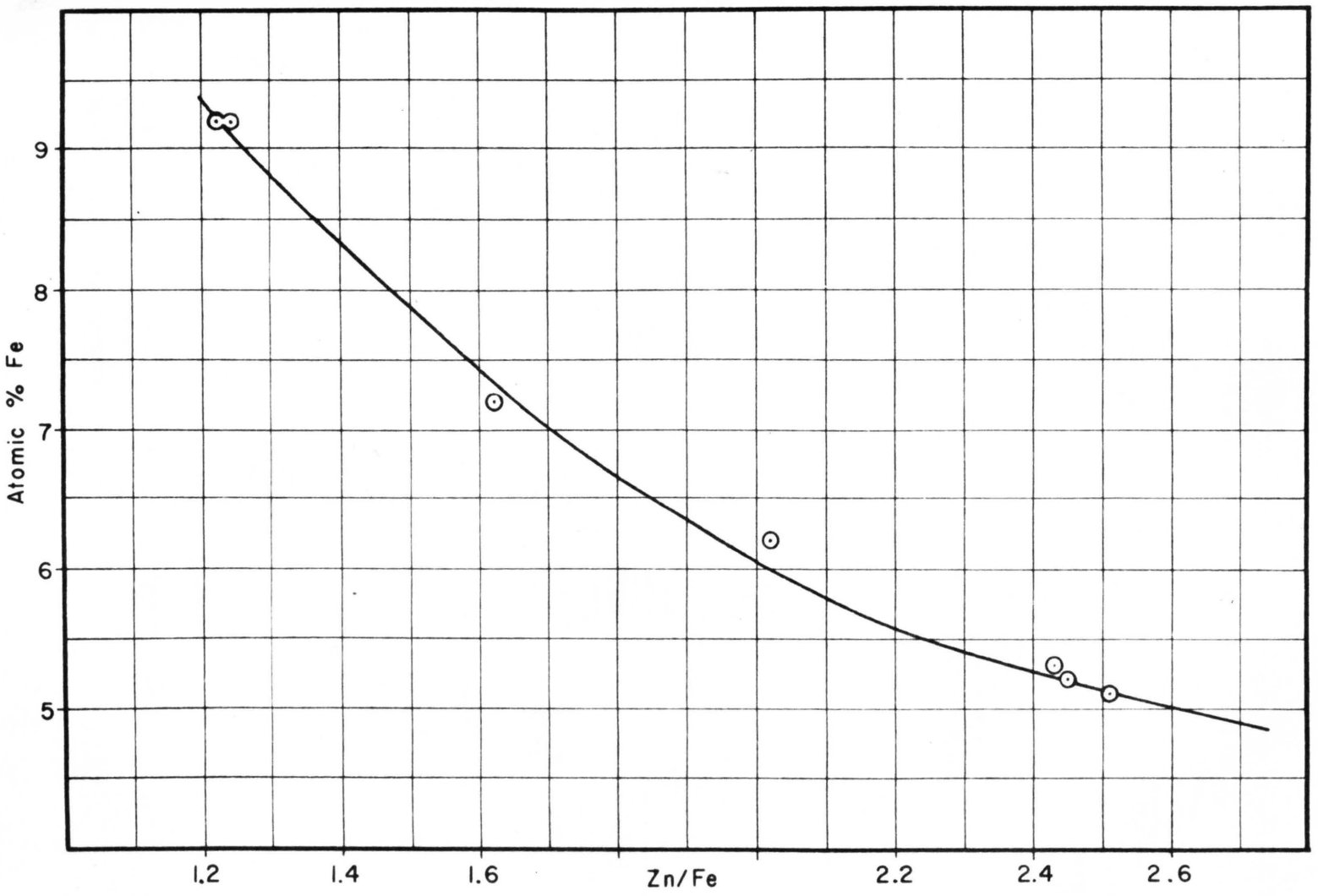


FIG. 3: CONVERSION CURVE FOR FLUORESCENT ZINC/IRON RATIOS TO ATOMIC PERCENT IRON

IV. STATEMENT AND APPLICATION OF THE RESULTS

The experimental results on the 12 samples from the 500 ft level (1-12) and the 13 samples from the 1500 ft level (13-25) are summarized in Table 4.

It is of interest to know what is the maximum error in terms of degrees Centigrade of the temperature of formation of the sphalerite that can be expected from this method of analysis. From the actual fluorescent standardization curve used for calculation of atomic percent iron, the farthest distance that any Zn/Fe fluorescent value lies from the curve is equivalent to 0.1 atomic percent iron. The average deviation is 0.06 atomic percent iron. Fig. 3 contains both the errors of the x-ray fluorescent and 'wet' quantitative analysis procedures. Thus the curve may be said to have an inherent error of $\pm$ 0.06 atomic percent iron. From Appendix I it may be seen that the average deviation of a Zn/Fe fluorescent ratio is $\pm$ 0.02. On Fig. 3 the latter value is equivalent to $\pm$ 0.1 atomic percent iron.

The maximum error for any unknown fluorescent ratio applied to Fig. 3 should be the sum of the error of the curve plus the error in the unknown ratio. The maximum error is then 0.16 atomic percent iron, or, keeping one significant figure, the maximum error is $\pm$ 0.2 atomic percent iron. On Fig. 1, 0.2 atomic percent iron is equivalent to 10°C on the steepest part of the curve. It seems reasonable that the temperatures given in Table 4 have an experimental accuracy of $\pm$ 10°C.

Table 4 shows the range of the temperature of formation of sphalerite to be 200°C at the Balmat No. 2 mine. It has been mentioned earlier that

water with 10 percent salinity has a critical temperature of 437°. If the pressure of formation of the sphalerite at Balmat is 2000 atm, 13 samples indicate a temperature of formation above the critical state. On Maps A and B of the 500 and 1500 ft levels are shown the locations of the samples used in this study. From the information in Table 4 and knowledge of the location of the samples, a contour map of isotherms may be constructed showing the variation of the temperature of formation on the two levels. Although the assumed pressure of formation may not be correct, the relative variation in temperature of formation should remain constant if the pressure of formation remains constant.

The scale of the two maps is approximately one inch to 200 ft, and the contour interval is 25 ft. The 1500 ft level appears to have three thermal peaks which may indicate three separate but overlapping loci of ore deposition. Two of the thermal peaks of the 1500 ft level have correlatives on the 500 ft level. An examination of the sphalerite west of sample 3 might reveal the third peak. It is interesting that a certain correlation may be made between the temperature of formation pattern of the 500 and 1500 ft levels.

Possibly the most interesting observation from Maps A and B is that while the temperature variation is roughly constant for each level (200° on the 500 ft level; 150° on the 1500 ft level) the maximum and minimum temperatures of formation on each level are similar (325°-525° on the 500 ft level; 350°-500° on the 1500 ft level). It must be remembered that a vertical distance of 1000 ft is represented while the radius of the ore body represented on each level is about 350 ft. Sample 3 and sample 5 are about 100 ft apart; yet, their difference in temperature of formation is

roughly 100°.

Brown (1947; p. 539) says, "Probably the microbreccias were formed, or at least received their significant shattering at or just following this period (granitic intrusion), and the ore deposition ensued soon or concomitantly." Previous to this Brown (1947; p. 532) said, "Structurally ore shoots tend to follow contacts between unlike wall rocks, particularly between limestone and diopside rock, or limestone and tremolite. Even within the area mapped as serpentinous diopside, narrow bands of purer limestone usually follow the ore on one wall or the other indicating that the ore body occupies a zone of compositional gradation."

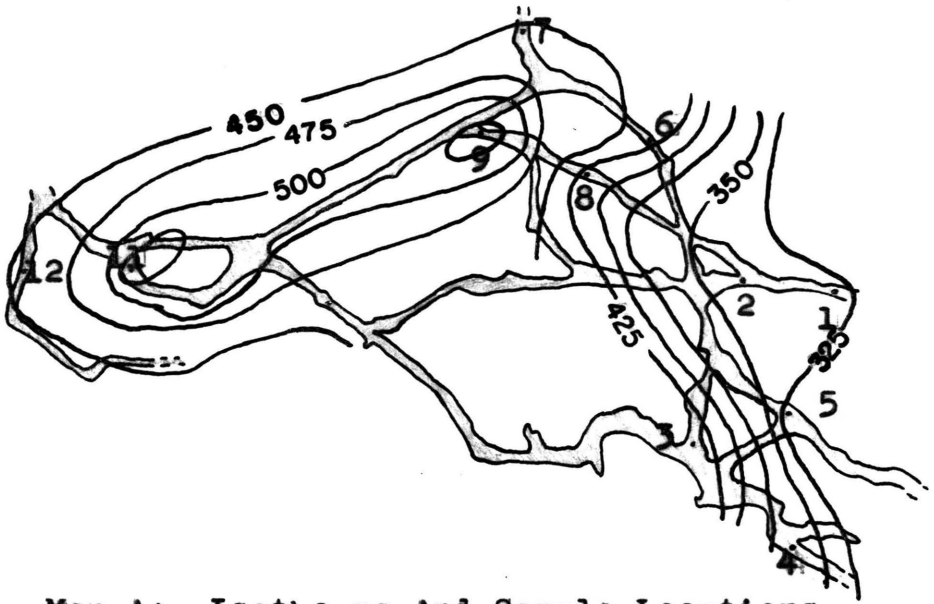
If the ore fluids were introduced rapidly into the microbrecciated zones and wall rock boundaries, the ore fluid might not have been given a chance to cool. If the permeability of the wall rock decreased laterally, the lateral movement of the ore fluid would be retarded and given more time to be cooled by the country rock over a given distance than in the central pipe. In this case some sphalerite might have been deposited because of the change of solubility with temperature, but the preference of the veins for calcite (see above) indicates basically a chemical control for deposition with permeability governing transport to the limestones.

The highest iron content sphalerites are found on the 500 ft level (Sa 9, 11). The author cannot envision an ore solution moving downward and cooling or upward and heating. This anomalous pattern might occur if:

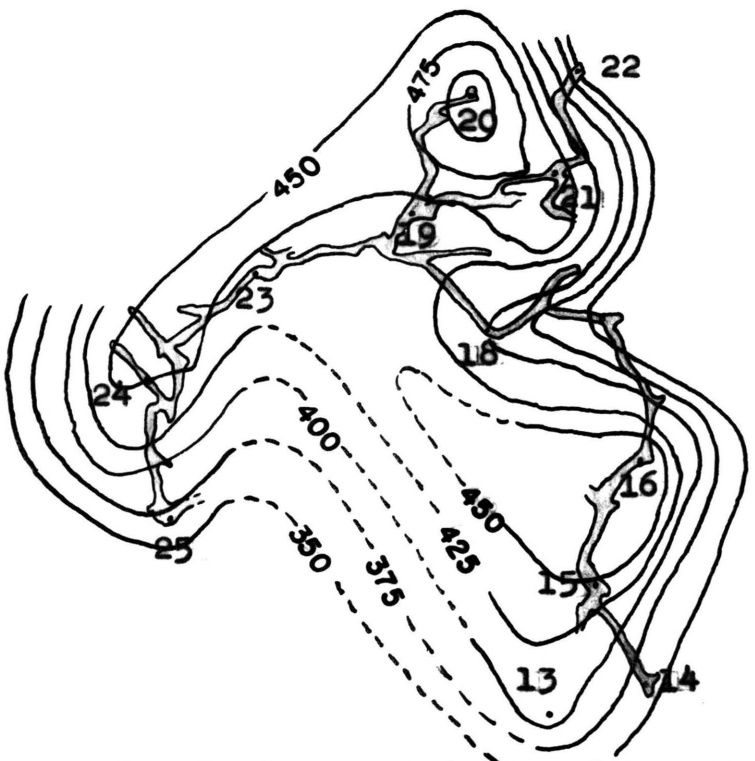
1. There was an abnormal drop in pressure between the two levels (1000 ft of rock load would approximate 70 atm). If the pressure on the 500 ft level were 1000 atm less than on the 1500 ft level, the temperature of formation on the 1500 ft level should be increased 25°.

Table 4: A Summary Of The Experimental Results

Sa.No.	Zn/Fe (Fluores.)	Zn/Fe (Wet)	Weight % Fe	Atomic % Fe	Temp. °C (1 atm)	Temp. °C (2000 atm)
1	2.63		4.5	4.9	280	330
2	2.54		4.6	5.1	290	340
3	1.79		6.2	6.8	380	430
4	2.43	12.6	(4.8)	(5.3)	310	360
5	2.72		4.3	4.8	270	320
6	1.83		6.1	6.5	390	440
7(?)	1.55		7.0	7.6	410	460
8(?)	2.12		5.4	5.9	360	410
9	1.22	7.0	(8.4)	(9.2)	475	525
10	1.95		5.8	6.3	350	460
11	1.24	7.0	(8.4)	(9.2)	475	525
12(?)	1.58		7.0	7.5	410	460
13	2.11		5.5	5.9	360	410
14a	2.29					
14b	1.53					
14c	2.29					
14(avg)	2.29		5.1	5.5	310	360
15	1.60		6.8	7.4	400	450
16	1.51		7.1	7.7	410	460
17	2.51	13.2	(4.7)	(5.1)	290	340
18	2.02	10.5	(5.7)	(6.2)	350	400
19	1.70		6.5	7.0	390	440
20	1.32		7.9	8.6	450	500
21	1.56		6.9	7.5	410	460
22a	2.45					
22b	2.44					
22c	2.35					
22d	2.47					
22(avg)	2.45	13.0	(4.8)	(5.2)	300	350
23	1.77		6.3	6.8	380	430
24a	1.61					
24b	1.60					
24c	1.62					
24d	1.47					
24e	1.64					
24(avg)	1.62	9.0	(6.7)	(7.2)	400	450
25	2.29		5.1	5.6	320	370



Map A: Isotherms And Sample Locations
On The 500 Ft. Level



Map B: Isotherms And Sample Locations
On The 1500 Ft. Level

PLAN VIEWS OF THE BALMAT NO. 2 MINE

2. The highest iron content sphalerites of the 1500 ft level escaped sampling.

3. There is an error in the quantitative analysis.

4. The difference in temperature is close to the limit of accuracy of the experimental method.

The answer to the apparent temperature rise may be a combination of all four of the factors mentioned above (average deviation in quantitative analysis was 0.2 atomic percent Fe or equivalent to 10°C.). The 500 level is not directly above the 1500 ft level so the direction of movement of the ore fluid was intermediate between vertical and horizontal.

An interesting problem would be to consider the effects a drop in temperature might have on an ore fluid in which all other factors remain constant. From Table 4 it may be seen that the highest iron content sphalerite has 8.5 wt percent Fe (525°), and the lowest iron content sphalerite contains 4.3 wt percent Fe. Hypothetically an ore fluid might be considered to have a composition of 8.3 wt percent iron and 91.7 wt percent ZnS. If this ore fluid deposited all the available ZnS at 525° and 2000 atm, all the available iron would enter the sphalerite lattice.

If this same ore fluid deposited the sphalerite at 320° and 2000 atm instead of at 525° only 4.3 wt percent Fe may exist in the sphalerite lattice, or there would be an excess of iron of 4.1 wt percent. One ton of ore would now consist of 4.1 wt percent Fe and 95.9 wt percent (Zn,Fe)S. This is equivalent to 82 lb of iron and 1918 lb of (Zn,Fe)S. If all the excess iron is deposited as pyrite 82 lb of iron is equivalent to 178 lb of pyrite. Thus our original deposit would consist of 178 lb of pyrite and 1918 lb of sphalerite or 2096 lb.

The density of pyrite is 5.0; the density of sphalerite is approximately 4.0. One cubic foot of pyrite would weigh 312 lb, and one cubic foot of sphalerite would weigh 249.6 lb. Then 178 lb of pyrite is equivalent to 0.57 cu ft, and 1918 lb of sphalerite is equivalent to 7.68 cu ft. Thus the ore body is 93 vol percent sphalerite and 7 vol percent pyrite. At the lower temperature, 2096 lb of ore would contain 178 lb of pyrite or 7 vol percent. No pyrite would be expected in the higher temperature deposit.

In a mine such as Balmat, more pyrite might be expected in the lower temperature portions of the ore body than in the higher temperature portions if only thermal control is considered. A statistical mineralographic study should indicate if this relationship exists. It might be that both high iron sphalerite and pyrite cannot be avoided in a deposit such as the one covered in this report. However, a choice might be able to be made between little pyrite and iron rich sphalerite or much pyrite with iron poor sphalerite. Undoubtedly other factors will influence the deposition of pyrite, also, such as the pH, change of solubility with temperature, and H_2S concentration. However, a more complete study might prove that the process covered above plays a significant role in the pyrite segregation in sphalerite deposits.

Later in this paper a means is presented of estimating the pressure-temperature conditions of sphalerite by combining the FeS-ZnS geothermometer with the two phase fluid inclusion thermometer. The sphalerite at the Balmat No. 2 appeared too well cleaved to place any confidence in the two phase inclusion method. There is no reason to disagree with Kullerud's assumption of 2000 atm which is certainly more probable than one atmosphere.

V. SPHALERITE: A PRESSURE-TEMPERATURE GAUGE

It has been mentioned that the solubility of iron in sphalerite is proportional not only to temperature but to pressure as well because the sphalerite lattice is expanded upon addition of iron. Fig. 4 shows the temperature-composition diagram for several different pressures. It may be seen that data can be obtained for a pressure-temperature curve for sphalerite of a particular iron content. The data for Fig. 4 is given in Table 5.

Table 5: Pressure-Temperature-Composition Data

T °K	1 atm	1000 atm	2000 atm	3000 atm	4000 atm	5000 atm
973	16.4	15.2	14.1	13.0	12.0	11.1
873	13.1	12.0	11.0	10.1	9.26	8.49
773	10.2	9.25	8.38	7.60	6.89	6.25
673	7.62	6.80	6.07	5.42	4.84	4.32
573	5.20	4.55	3.98	3.48	3.05	2.67
473	3.36	2.86	2.43	2.07	1.76	1.50
412	2.80	2.33	1.94	1.61	1.34	1.11

Columns one and two in Table 5 are taken from columns one and seven of Table 1. The values for atomic percent content in the succeeding columns were derived from the formula given by Kullerud (1953; p. 105):

$$x_1 = xe^{\left(\frac{\Delta F - \Delta F_1}{RT}\right)}$$

and

$$\Delta F - \Delta F_1 = \Delta V(P - P_1)$$

thus

$$\ln(x_1) - \ln(x) = \Delta V(P - P_1)/(RT)$$

x_1 is the atomic percent iron at the lower pressure

x is the atomic percent iron at the higher pressure

ΔV is the change in volume from pure sphalerite (39.333 A^3) to the volume that FeS should have with the sphalerite structure (40.125 A^3).

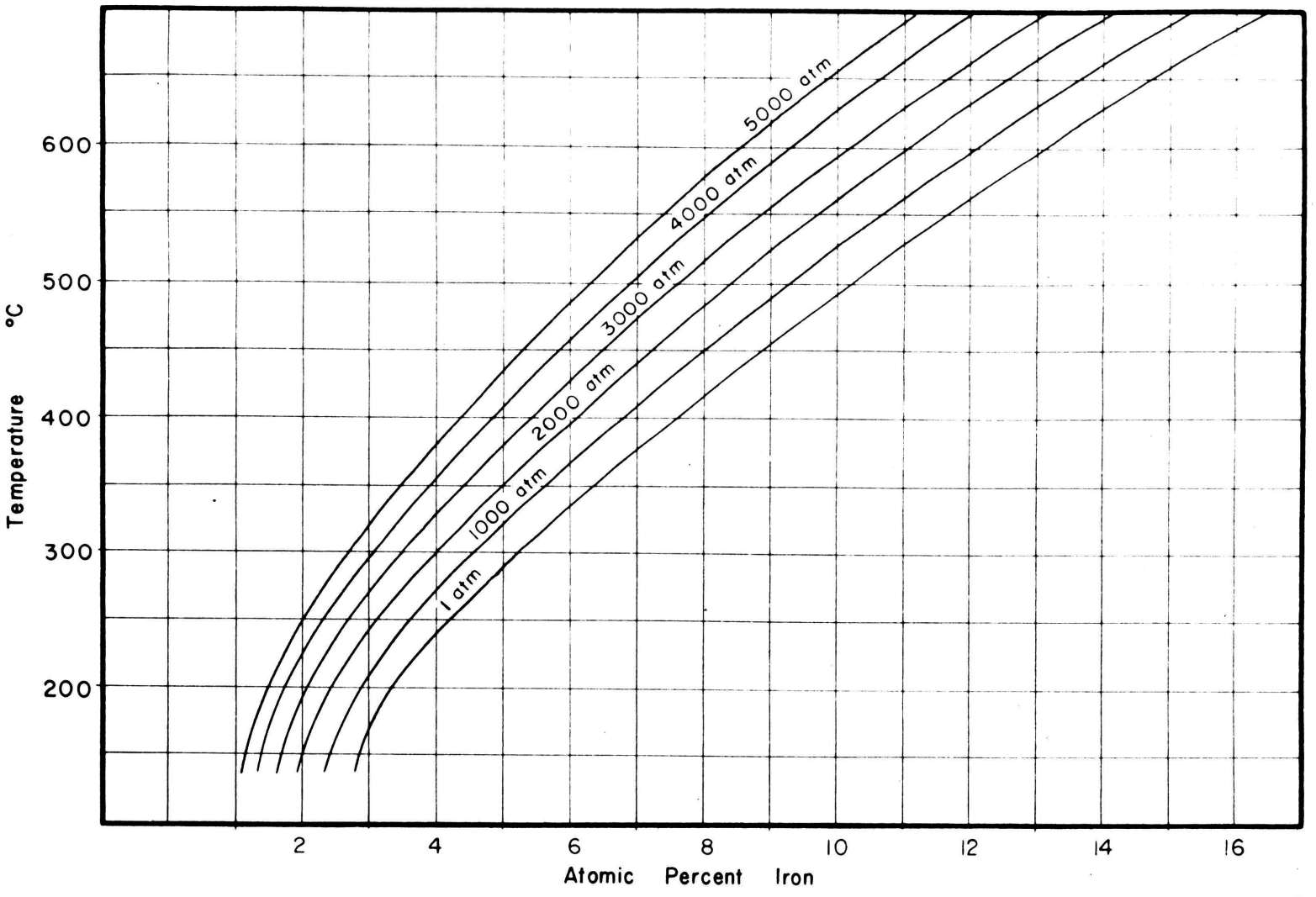


FIG. 4: TEMPERATURE - COMPOSITION DIAGRAM IN THE FeS-ZnS SYSTEM FOR SEVERAL PRESSURES
(Recalculated From Kullerud Weight Percent Data; 1953, p. 98)

P_1 is the lower pressure

P is the higher pressure

The assumptions made in calculating the pressure from the above formulas are:

1. The solution of iron in sphalerite is ideal.
2. The molar volume of sphalerite type FeS is approximately correct (this volume was found by extrapolating known expansions of the sphalerite lattice by FeS to the point that all the ZnS has been replaced by FeS) (See Kullerud; 1953, p.92).
3. Errors in the non-ideality of the solid solution will be discounted by keeping pressure calculations to 1000 atm increments.

The pressure effect must also be taken into account in the application of two-phase inclusions to geothermometry, although this is not usually done. Kennedy (1950; p. 540) has shown that pressure will definitely effect the degree of filling of inclusions because of the compressibility of water. Kennedy's figure is redrawn and presented as Fig. 5a. The degree of filling is usually measured in geology by determining the temperature of disappearance of the two phase boundary in the inclusion. Ingerson (1947; p. 378) has shown that the salinity of the ore solution would affect the apparent temperature of formation as shown in Fig. 5b. The higher the saline content the less compressible the solution so the higher the temperature for the same degree of filling. By measuring the degree of filling at the temperature of disappearance of the two phase boundary this difference in compressibility with salinity is discounted. Some error will be introduced in pressure calculations from Kennedy's pressure correction graph because it was calculated for pure water. A good estimate should be obtained of a pressure-temperature curve for any one temperature of disappearance of the two phase inclusion boundary.

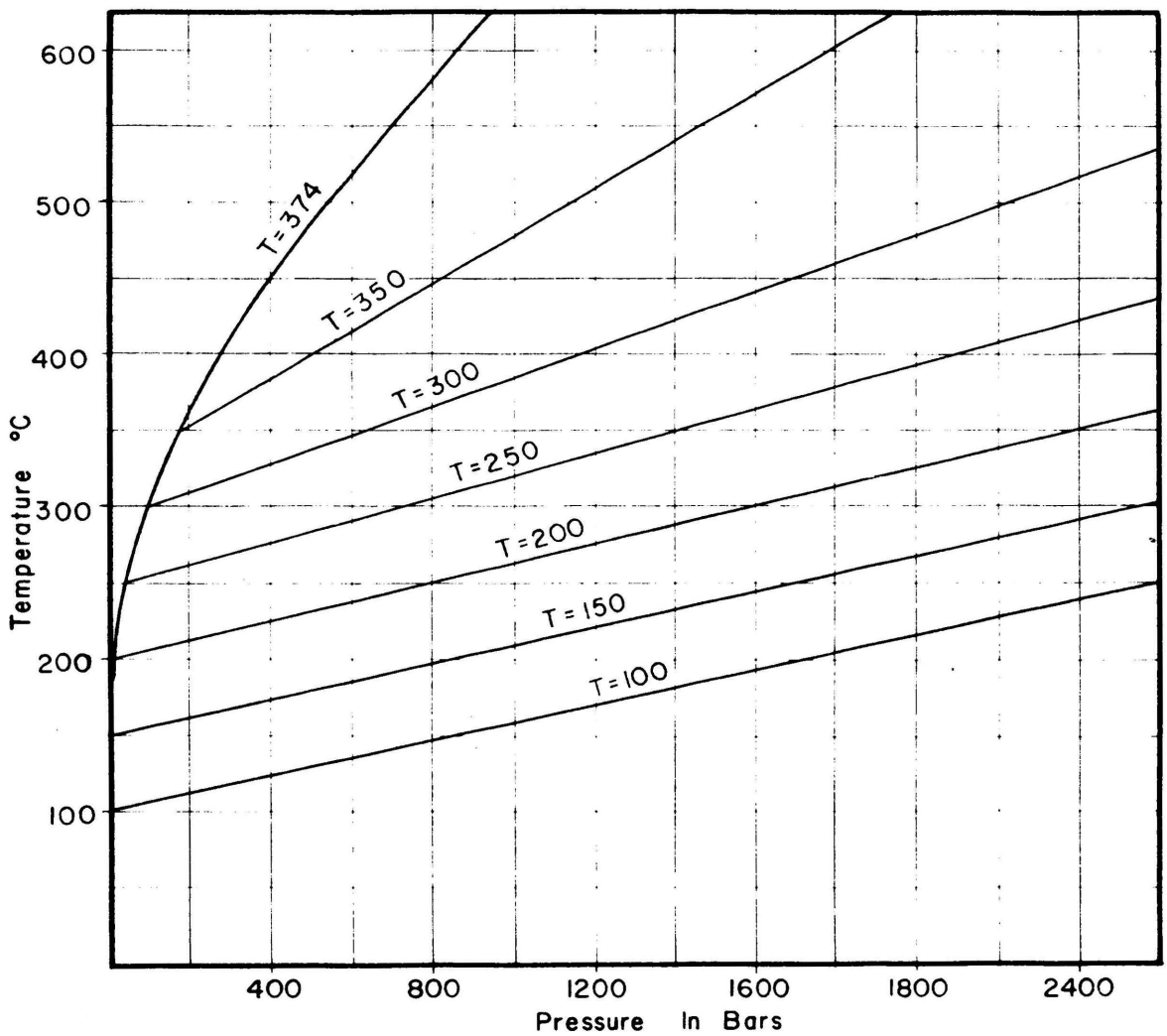


FIG. 5a: PRESSURE-TEMPERATURE DIAGRAM FOR THE TEMPERATURE OF DISAPPEARANCE AT 1 ATM OF THE TWO PHASE BOUNDARY OF WATER-VAPOR INCLUSIONS

Redrawn With Modification From Kennedy; 1950, p. 540

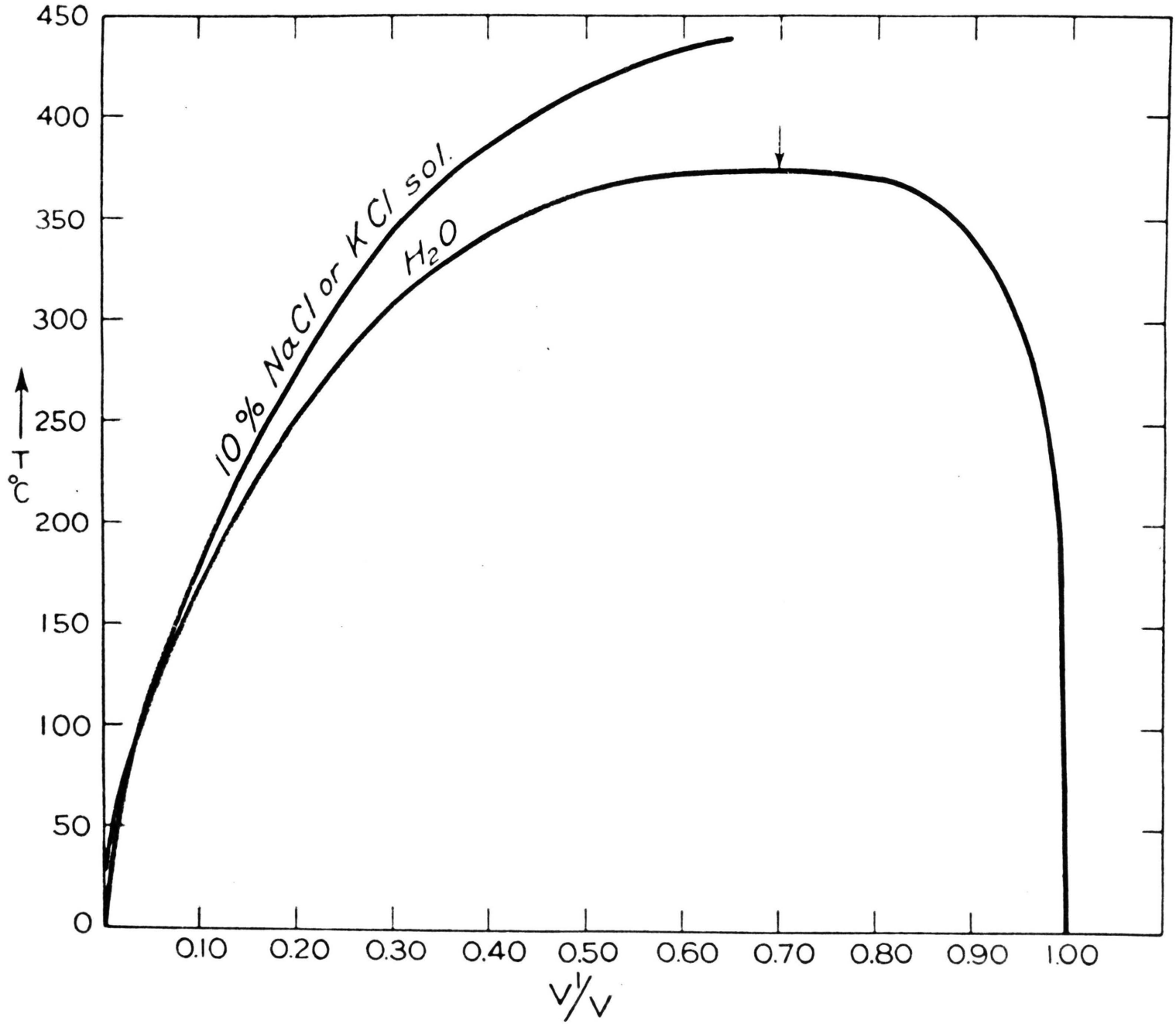


Fig. 5b: Temperature Of Disappearance vs. Degree Of Filling

The assumption that the inclusions and the (Zn,Fe)S crystal formed at the same temperature and pressure seems valid (disregarding secondary inclusion). Thus if we plot the pressure-temperature curves of a sphalerite with fluid inclusions for the atomic percent iron found in the sphalerite and the disappearance of the two phase inclusions, the pressure temperature curves should intersect at the pressure and temperature of formation. A hypothetical example of this pressure temperature gauge is given for a sphalerite of six atomic percent iron and temperature of disappearance of the two phase inclusion of 300°C. It will be seen in Fig. 6 that the indicated temperature and pressure of formation is 350°C and 700 atm. It must be remembered that all of the assumptions that influence the FeS-ZnS and fluid inclusion geothermometers also apply to the sphalerite pressure-temperature gauge.

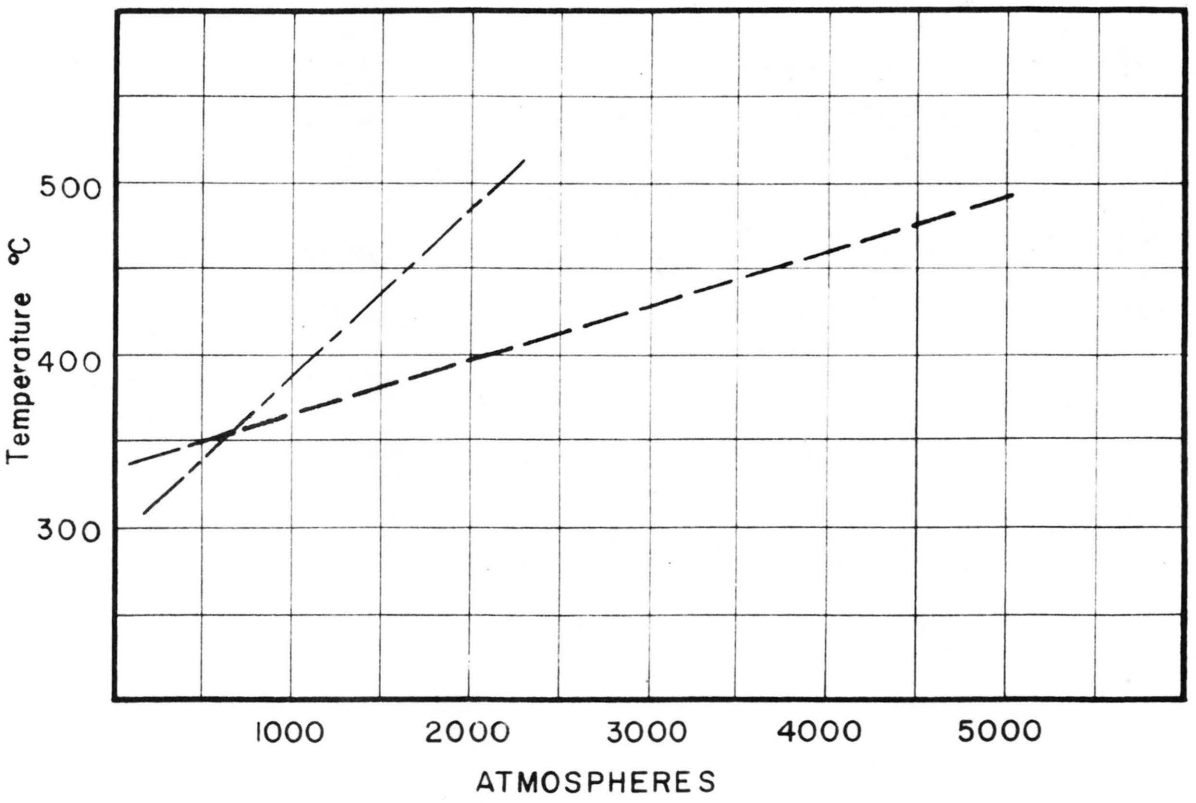


FIG. 6: HYPOTHETICAL APPLICATION OF THE SPHALERITE PRESSURE-TEMPERATURE GAUGE

——— Sphalerite of six atomic percent iron
– – – – Sphalerite in which the two phase boundary disappears at 300°C

VI. SUMMARY AND CONCLUSIONS

Twelve samples from the 500 ft level and 13 samples from the 1500 ft level from the Balmat No. 2 mine were analyzed for iron content of sphalerite. The results of the quantitative analysis were applied to the FeS-ZnS geothermometer as worked out by Kullerud. A range in temperature of formation of 200°C for the deposit was found. The temperature variation pattern may be roughly correlated between the two levels. A few more samples would be desirable for more isothermal control.

A relatively accurate method of measuring the pressure-temperature conditions of sphalerite formation is presented. The pressure-temperature conditions are determined by drawing the pressure-temperature curves for the iron content of sphalerite and the degree of filling of two phase inclusions. The intersection of the two pressure-temperature curves should indicate the pressure and temperature of formation of the sphalerite because the inclusion and the sphalerite crystal formed at about the same conditions. The pressure temperature gauge will only apply when the assumptions used in the FeS-ZnS and fluid inclusion geothermometers are valid.

From this study it may be concluded that deposition of sphalerite in an ore body may take place under widely varying sets of pressure-temperature conditions. The quoting of the temperature of formation of the minerals from a mine from one or two analyses is invalid. The pattern of change in the temperature of formation may be roughly correlated from level to level in such a mine as the Balmat No. 2. The variation in temperature was mostly lateral (roughly 1°/ft ?). The Balmat deposit would be classified as hypothermal following Lindgren. If the estimate of pressure is

conservative, most of the water present must have been in the super-critical state even assuming 10 percent salinity.

There is a suggestion of three distinct pipes and/or stages of ore fluid introduction. A more complete study of the three ore bodies including age determinations should prove interesting. Another study of interest would be to examine the variation of the wall rock mineralogy with the sphalerite temperature of formation.

APPENDIX I Calculation of Zn/Fe Fluorescent Ratios

Columns a., b., and c. are the cumulative planimeter relative area measurements underneath a fluorescent peak. The number immediately above the bar is the sum of 'x' relative area measurements (usually five). The number beneath the bar is obtained by dividing the latter number by 'x'.

Sample No. 1

Relative areas						Averages
a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe	Zn:
0.72	0.68	0.70	0.27	0.27	0.26	0.716 + 0.004
1.43	1.41	1.40	0.55	0.55	0.53	0.718 + 0.006
2.15	2.14	2.11	0.82	0.84	0.80	0.702 - 0.010
2.88	2.88	2.81	1.08	1.11	1.06	0.712 ± 0.007
3.58	3.61	3.51	1.36	1.37	1.33	
0.716	0.718	0.702	0.272	0.274	0.266	Fe:
						0.272 + 0.001
						0.274 + 0.003
						0.266 - 0.005
						0.271 ± 0.003

Zn/Fe = 0.712/0.271 = 2.63 ± 0.01

Sample No. 2

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe	Zn:
0.73	0.77	0.72	0.30	0.31	0.26	0.728 - 0.015
1.46	1.54	1.44	0.57	0.62	0.52	0.766 + 0.023
2.18	2.32	2.16	0.85	0.95	0.82	0.735 + 0.008
2.91	3.05	2.94	1.16	1.23	1.13	0.743 ± 0.015
3.64	3.83	3.67	1.45	1.55	1.40	
0.728	0.766	0.734	0.290	0.310	0.280	Fe:
						0.290 - 0.003
						0.310 + 0.017
						0.280 - 0.013
						0.293 ± 0.011

Zn/Fe = 0.743/0.293 = 2.54 ± 0.02

Sample No. 3

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe	Zn:
0.73	0.75	0.75	0.42	0.42	0.41	0.712 - 0.003
1.42	1.44	1.50	0.82	0.80	0.82	0.704 - 0.011
2.13	2.11	2.23	1.23	1.20	1.24	0.730 + 0.015
2.85	2.82	2.93	1.63	1.57	1.63	0.715 ± 0.010
3.56	3.52	3.65	2.03	1.96	2.00	
0.712	0.704	0.730	0.406	0.392	0.40	Fe:
						0.406 + 0.007
						0.392 - 0.007
						0.400 + 0.001
						0.399 ± 0.005

Zn/Fe = 0.715/0.399 = 1.79 ± 0.01

APPENDIX I (Continued)

Sample No. 4

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.60	0.65	0.62	0.25	0.25	0.26
1.20	1.26	1.23	0.50	0.52	0.59
1.79	1.82	1.84	0.74	0.76	0.74
2.41	2.45	2.45	0.99	1.03	0.98
3.02	3.05	3.08	1.25	1.28	1.24
0.604	0.610	0.616	0.250	0.256	0.248

Zn:

0.604 - 0.006
0.610 - 0.000
0.616 + 0.006
0.610 ± 0.004

Fe:

0.250 - 0.001
0.256 + 0.005
0.248 - 0.003
0.251 ± 0.003

Zn/Fe = 0.610/0.251 = 2.43 ± 0.01

Sample No. 5

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.45	0.48	0.48	0.17	0.18	0.16
0.95	0.95	0.93	0.35	0.35	0.34
1.37	1.42	1.38	0.52	0.54	0.51
1.85	1.89	1.91	0.69	0.73	0.69
2.34	2.37	2.37	0.86	0.91	0.86
2.85			1.02	1.10	1.02
0.474	0.474	0.474	0.170	0.183	0.170

Zn:

0.474

Fe:

0.170 - 0.004
0.183 + 0.009
0.170 - 0.004
0.174 ± 0.006

Zn/Fe = 0.474/0.174 = 2.72 ± 0.01

Sample No. 6

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.44	0.45	0.51	0.26	0.27	0.27
0.90	0.96	1.00	0.54	0.53	0.53
1.36	1.46	1.46	0.82	0.81	0.81
1.85	1.93	1.96	1.07	1.05	1.05
2.32	2.43	2.46	1.32	1.31	1.32
0.464	0.486	0.492	0.264	0.262	0.264

Zn:

0.462 - 0.018
0.492 + 0.012
0.486 + 0.006
0.480 ± 0.012

Fe:

0.264 + 0.001
0.262 - 0.001
0.264 + 0.001
0.263 ± 0.001

Zn/Fe = 0.480/0.263 = 1.83 ± 0.01

APPENDIX I (Continued)

Sample No. 7

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.97	0.98	1.02	0.66	0.63	0.70
1.98	1.98	2.05	1.32	1.26	1.38
2.98	2.98	3.07	2.00	1.89	2.08
3.97	3.98	4.07	2.68	2.54	2.78
4.96	5.02	5.12	3.34	3.29	3.46
0.992	1.004	1.024	0.668	0.658	0.692

Zn:

0.992 - 0.015
1.004 - 0.003
1.024 + 0.017
1.007 ± 0.012

Fe:

0.668 - 0.005
0.658 - 0.015
0.692 + 0.019
0.673 ± 0.013

Zn/Fe = 1.007/0.673 = 1.50 ± 0.02

Sample No. 8

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.43	1.48	1.41	0.73	0.72	0.67
2.86	2.92	2.82	1.40	1.42	1.34
4.30	4.37	4.28	2.05	2.05	2.00
5.73	5.85	5.74	2.74	2.77	2.67
7.17	7.31	7.15	3.43	3.47	3.35
1.434	1.462	1.430	0.686	0.694	0.670

Zn:

1.434 - 0.008
1.462 + 0.020
1.430 - 0.012
1.442 ± 0.013

Fe:

0.686 + 0.003
0.694 + 0.011
0.670 - 0.013
0.683 ± 0.010

Zn/Fe = 1.442/0.683 = 2.12 ± 0.02

Sample No. 9

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.57	0.56	0.57	0.43	0.42	0.44
1.14	1.16	1.16	0.86	0.86	0.91
1.70	1.74	1.71	1.28	1.28	1.36
2.27	2.32	2.27	1.71	1.73	1.81
2.85	2.90	2.85	2.13	2.15	2.24
0.570	0.580	0.570	0.426	0.430	0.448

Zn:

0.570 - 0.003
0.580 + 0.007
0.570 - 0.003
0.573 ± 0.004

Fe:

0.426 - 0.009
0.430 - 0.003
0.448 + 0.013
0.435 ± 0.008

Zn/Fe = 0.573/0.435 = 1.22 ± 0.01

APPENDIX I (Continued)

Sample No. 10

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.31	1.25	1.27	0.65	0.66	0.63
2.62	2.46	2.55	1.32	1.33	1.30
3.91	3.73	3.82	1.95	1.97	1.96
5.16	5.01	5.07	2.56	2.63	2.59
6.45	6.28	6.34	3.31	3.26	3.24
1.290	1.256	1.268	0.662	0.652	0.648

Zn/Fe = 1.271/0.654 = 1.95 ± 0.02

Zn:

1.290 + 0.019
1.256 - 0.015
1.268 - 0.002
1.271 ± 0.018

Fe:

0.662 + 0.008
0.652 - 0.002
0.648 - 0.006
0.654 ± 0.005

Sample No. 11

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.25	1.21	1.27	0.98	1.02	1.01
2.46	2.43	2.54	1.97	2.02	2.04
3.73	3.68	3.78	2.95	3.01	3.01
4.94	4.91	5.08	3.96	4.00	4.06
6.14	6.13	6.36	4.98	5.02	5.07
1.228	1.226	1.272	0.998	1.004	1.014

Zn/Fe = 1.242/1.005 = 1.24 ± 0.03

Zn:

1.228 - 0.014
1.226 - 0.016
1.272 + 0.030

Fe:

0.998 - 0.007
1.004 - 0.001
1.014 + 0.009
1.005 ± 0.006

Sample No. 12

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.98	0.98	0.96	0.63	0.63	0.64
1.97	1.92	2.05	1.25	1.25	1.24
2.96	2.91	3.03	1.88	1.83	1.87
3.95	3.91	4.01	2.50	2.44	2.52
4.94	4.87	5.02	3.14	3.08	3.13
0.988	0.974	1.004	0.628	0.616	0.626

Zn/Fe = 0.989/0.623 = 1.58 ± 0.02

Zn:

0.988 - 0.001
0.974 - 0.015
1.004 + 0.015
0.989 ± 0.010

Fe:

0.628 + 0.005
0.616 - 0.007
0.626 + 0.003
0.623 ± 0.005

APPENDIX I (Continued)

Sample No. 13

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.38	1.35	1.37	0.67	0.67	0.65
2.75	2.74	2.76	1.33	1.32	1.28
4.14	3.10	4.13	1.97	1.97	1.94
5.52	4.44	5.51	2.63	2.63	2.61
6.90	5.83	6.89	3.26	3.28	3.26
1.380	1.366	1.378	0.652	0.656	0.652

Zn/Fe = 1.375/0.653 = 2.11

Zn:

1.380 + 0.005
1.368 - 0.007
1.378 + 0.003
1.375 ± 0.005

Fe:

0.652 - 0.001
0.656 + 0.003
0.652 - 0.001
0.653 ± 0.002

Sample No. 14a (Engineer's Day Morning)

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.61	0.64	No	0.28	0.27	0.27
1.24	1.28	Good	0.57	0.55	0.53
1.86	1.92		0.85	0.83	0.82
2.46	2.55		1.12	1.09	1.09
3.08	3.19		1.39	1.36	1.37
0.616	0.638		0.278	0.272	0.274

Zn/Fe = 0.627/0.275 = 2.29 ± 0.01

Zn:

0.616 - 0.011
0.638 + 0.011
0.627 ± 0.011

Fe:

0.278 + 0.003
0.272 - 0.003
0.274 - 0.001
0.275 ± 0.002

Sample No. 14b (Engineer's Day Afternoon)

a. Zn	b. Zn	a. Fe	b. Fe	
0.57	0.57	0.23	0.23	
1.18	1.15	0.45	0.45	No more data
1.73	1.75	0.67	0.69	could be
2.30	2.33	0.89	0.93	obtained.
2.85	2.90	1.12	1.15	
0.570	0.580	0.224	0.230	

Zn/Fe = 0.575/0.227 = 2.53 ± 0.01

Zn:

0.570
0.580
0.575 ± 0.005

Fe:

0.224
0.230
0.227 ± 0.003

APPENDIX I (Continued)

Sample No. 14c (After 9:00 pm on Engineer's Day)

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.69	0.71	0.65	0.29	0.27	0.32
1.39	1.40	1.31	0.58	0.55	0.61
2.09	2.08	1.96	0.92	0.84	0.92
2.78	2.75	2.64	1.23	1.12	1.22
3.46	3.43	3.30	1.52	1.41	1.51
0.692	0.686	0.660	0.304	0.282	0.302

Zn:

$0.692 + 0.013$
$0.686 + 0.007$
$0.660 - 0.019$
0.679 ± 0.013

Fe:

$0.304 + 0.008$
$0.282 - 0.014$
$0.302 + 0.006$
0.296 ± 0.008

$Zn/Fe = 0.679/0.296 = 2.29 \pm 0.02$

Sample No. 15

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.52	0.54	0.55	0.34	0.35	0.35
1.06	1.10	1.09	0.68	0.68	0.71
1.63	1.63	1.63	1.00	1.02	1.05
2.20	2.15	2.16	1.32	1.35	1.41
2.73	2.69	2.72	1.66	1.69	1.76
0.546	0.538	0.544	0.332	0.338	0.352

Zn:

$0.546 + 0.003$
$0.538 - 0.005$
$0.544 + 0.001$
0.543 ± 0.003

Fe:

$0.332 - 0.009$
$0.338 - 0.003$
$0.352 + 0.011$
0.341 ± 0.007

$Zn/Fe = 0.543/0.341 = 1.60 \pm 0.01$

Sample No. 16

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.60	0.53	0.55	0.40	0.36	0.37
1.14	1.05	1.10	0.77	0.72	0.71
1.65	1.60	1.66	1.12	1.06	1.05
2.22	2.14	2.18	1.46	1.41	1.40
2.77	2.66	2.75	1.83	1.80	1.72
0.554	0.532	0.550	0.366	0.360	0.356

Zn:

$0.554 + 0.009$
$0.532 - 0.013$
$0.550 + 0.005$
0.545 ± 0.009

Fe:

$0.366 + 0.005$
$0.360 - 0.001$
$0.356 - 0.005$
0.361 ± 0.004

$Zn/Fe = 0.545/0.361 = 1.51 \pm 0.01$

APPENDIX I (Continued)

Sample No. 17

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.57	0.55	0.58	0.22	0.22	0.22
1.13	1.11	1.14	0.45	0.44	0.45
1.68	1.65	1.72	0.68	0.68	0.66
2.23	2.24	2.26	0.90	0.92	0.89
2.80	2.83	2.83	1.13	1.15	1.10
0.560	0.566	0.566	0.226	0.230	0.220

Zn/Fe = 0.564/0.225 = 2.51 ± 0.01

Zn:

0.560 - 0.004
0.566 + 0.002
0.566 + 0.002
0.564 ± 0.003

Fe:

0.226 + 0.001
0.230 + 0.005
0.220 - 0.005
0.225 ± 0.004

Sample No. 18

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.55	0.54	0.52	0.25	0.28	0.28
1.08	1.09	1.05	0.52	0.53	0.53
1.63	1.64	1.59	0.79	0.80	0.79
2.15	2.17	2.12	1.06	1.08	1.05
2.68	2.72	2.65	1.32	1.34	1.31
0.536	0.544	0.530	0.264	0.268	0.262

Zn/Fe = 0.537/0.265 = 2.02 ± 0.01

Zn:

0.536 - 0.001
0.544 + 0.007
0.530 - 0.007
0.537 ± 0.005

Fe:

0.264 - 0.001
0.268 + 0.003
0.262 - 0.003
0.265 ± 0.002

Sample No. 19

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.41	1.44	1.44	0.84	0.84	0.82
2.78	2.85	2.84	1.70	1.71	1.66
4.17	4.26	4.27	2.52	2.55	2.48
5.57	5.71	5.68	3.35	3.37	3.22
6.95	7.14	7.10	4.19	4.21	4.13
1.390	1.426	1.420	0.838	0.842	0.826

Zn/Fe = 1.412/0.835 = 1.70 ± 0.02

Zn:

1.390 - 0.022
1.426 + 0.014
1.420 + 0.008
1.412 ± 0.015

Fe:

0.838 + 0.003
0.842 + 0.007
0.826 - 0.009
0.835 ± 0.006

APPENDIX I (Continued)

Sample No. 20

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.45	1.45	1.42	1.15	1.05	1.11
2.89	2.86	2.86	2.19	2.15	2.22
4.32	4.30	4.32	3.25	3.23	3.78
5.73	5.73	5.75	4.35	4.33	4.38
7.16	7.10	7.19	5.42	5.37	5.45
1.432	1.420	1.438	1.084	1.074	1.090

Zn/Fe = 1.430/1.083 = 1.32 ± 0.01

Zn:

1.432 + 0.002
1.420 - 0.010
1.438 + 0.008
1.430 ± 0.007

Fe:

1.084 + 0.001
1.074 - 0.009
1.090 + 0.007
1.083 ± 0.006

Sample No. 21

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.18	1.17	1.21	0.77	0.75	0.77
2.34	2.36	2.42	1.56	1.50	1.56
3.54	3.53	3.61	2.33	2.24	2.25
4.73	4.73	4.77	3.07	3.00	3.00
5.94	5.92	5.94	3.82	3.78	3.89
1.188	1.184	1.188	0.764	0.756	0.758

Zn/Fe = 1.187/0.759 = 1.56 ± 0.01

Zn:

1.188 + 0.001
1.184 - 0.003
1.188 + 0.001
1.187 ± 0.002

Fe:

0.764 + 0.005
0.756 - 0.003
0.758 - 0.001
0.759 ± 0.003

Sample No. 22a

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.85	0.85	0.84	0.34	0.34	0.35
1.70	1.74	1.68	0.70	0.68	0.70
2.51	2.52	2.54	1.02	1.00	1.06
3.36	3.37	3.40	1.37	1.34	1.42
4.21	4.23	4.23	1.72	1.68	1.78
0.842	0.846	0.846	0.344	0.336	0.356

Zn/Fe = 0.845/0.345 = 2.45 ± 0.01

Zn:

0.842 - 0.003
0.846 + 0.001
0.846 + 0.001
0.845 ± 0.002

Fe:

0.344 - 0.001
0.336 - 0.009
0.356 + 0.011
0.345 ± 0.007

APPENDIX I (Continued)

Sample No. 22b

a. Zn	b. Zn	c. Zn	d. Zn	a. Fe	b. Fe	c. Fe
1.21	1.21	1.29	1.21	0.50	0.51	0.50
2.43	2.40	2.57	2.42	0.98	1.00	0.98
3.57	3.61	3.85	3.65	1.47	1.48	1.51
4.71	4.82	5.00	4.84	1.95	1.96	2.01
6.00	6.02	6.14	6.01	2.45	2.46	2.50
1.200	1.204	1.228	1.202	0.490	0.492	0.500

Zn:

1.200 - 0.009
1.204 - 0.005
1.228 + 0.017
1.202 - 0.007
1.209 ± 0.009

Fe:

0.490 - 0.004
0.492 - 0.002
0.500 + 0.006
0.494 ± 0.004

Zn/Fe = 1.209/0.494 = 2.44 ± 0.01

Sample No. 22c

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.01	1.06	1.03	0.43	0.44	0.42
2.03	2.06	2.04	0.87	0.86	0.83
3.01	3.13	3.06	1.31	1.30	1.25
4.05	4.14	4.05	1.75	1.73	1.66
5.03	5.13	5.03	2.19	2.16	2.11
1.006	1.022	1.006	0.438	0.432	0.422

Zn:

1.006 - 0.005
1.022 + 0.011
1.006 - 0.005
1.011 ± 0.007

Fe:

0.438 + 0.007
0.432 + 0.001
0.422 - 0.009
0.431 ± 0.006

Zn/Fe = 1.011/0.431 = 2.35 ± 0.01

Sample No. 22d

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.65	0.68	0.63	0.26	0.25	0.27
1.31	1.32	1.28	0.52	0.53	0.55
1.94	1.97	1.91	0.77	0.78	0.81
2.59	2.64	2.53	1.03	1.05	1.06
3.24	3.29	3.14	1.28	1.32	1.33
0.648	0.658	0.634	0.256	0.264	0.266

Zn:

0.648 + 0.001
0.658 + 0.011
0.634 - 0.013
0.647 ± 0.008

Fe:

0.256 - 0.006
0.264 + 0.002
0.266 + 0.004
0.262 ± 0.004

Zn/Fe = 0.647/0.262 = 2.47 ± 0.01

APPENDIX I (Continued)

Sample No. 23

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
0.69	0.65	0.68	0.40	0.38	0.38
1.36	1.32	1.35	0.77	0.75	0.77
1.94	1.98	2.02	1.16	1.11	1.15
2.62	2.64	2.71	1.55	1.48	1.54
3.39	3.28	3.39	1.93	1.84	1.91
0.678	0.656	0.678	0.386	0.368	0.382

Zn:

0.678 + 0.007
0.656 - 0.015
0.678 + 0.007
0.671 ± 0.010

Fe:

0.386 + 0.007
0.368 - 0.011
0.382 + 0.003
0.379 ± 0.007

Zn/Fe = 0.671/0.379 = 1.77 ± 0.02

Sample No. 24a

a. Zn	b. Zn	a. Fe	b. Fe
0.94	0.97	0.58	0.61
1.92	1.87	1.17	1.18
2.87	2.85	1.76	1.80
3.85	3.80	2.36	2.36
4.80	4.75	2.95	2.96
0.960	0.950	0.590	0.592

Zn:

0.955 ± 0.005

Fe:

0.591 ± 0.001

Zn/Fe = 0.955/0.591 = 1.62 ± 0.01

Sample No. 24b

a. Zn	b. Zn	a. Fe	b. Fe
0.96	0.95	0.60	0.61
1.92	1.91	1.20	1.22
2.89	2.87	1.81	1.81
3.85	3.86	2.41	2.42
4.81	4.82	3.01	3.02
0.962	0.964	0.602	0.604

Zn:

0.963 ± 0.001

Fe:

0.603 ± 0.001

Zn/Fe = 0.963/0.603 = 1.60

APPENDIX I (Continued)

Sample No. 24c

a. Zn	b. Zn	c. Zn	a. Fe	b. Fe	c. Fe
1.02	1.06	1.04	0.64	0.65	0.61
2.01	2.08	2.07	1.28	1.31	1.24
3.01	3.12	3.13	1.95	1.96	1.85
4.03	4.15	4.17	2.56	2.61	2.50
5.05	5.12	5.21	3.18	3.25	3.15
1.010	1.024	1.042	0.636	0.650	0.630

Zn: 1.010 - 0.015
1.042 + 0.017
1.024 - 0.001
1.025 ± 0.011

Fe: 0.636 - 0.003
0.650 + 0.011
0.630 - 0.009
0.639 ± 0.008

Zn/Fe = 1.025/0.639 = 1.61 ± 0.02

Sample No. 24d

a. Zn	b. Zn	a. Fe	b. Fe
1.16	1.17	0.80	0.86
2.38	2.35	1.62	1.67
3.56	3.58	2.42	2.47
4.76	4.78	3.20	3.31
5.95	5.96	3.99	4.15
1.190	1.192	0.798	0.830

Zn: 1.191 ± 0.001

Fe: 0.814 ± 0.016

Zn/Fe = 1.191/0.814 = 1.47 ± 0.02

Sample No. 24e

a. Zn	b. Zn	c. Zn	a. Fe	b. Ve	c. Fe
0.55	0.54	0.57	0.32	0.35	0.34
1.11	1.08	1.13	0.66	0.71	0.68
1.65	1.64	1.70	0.98	1.05	1.03
2.20	2.21	2.25	1.31	1.40	1.37
2.79	2.76	2.80	1.64	1.73	1.73
0.558	0.552	0.560	0.328	0.346	0.346

Zn: 0.558 + 0.001
0.552 - 0.005
0.560 + 0.003
0.557 ± 0.003

Fe: 0.328 - 0.012
0.346 + 0.006
0.346 + 0.006
0.340 ± 0.008

Zn/Fe = 0.557/0.340 = 1.64 ± 0.010

Sample No. 25

a. Zn	b. Zn	a. Fe	b. Fe
1.56	1.48	0.71	0.76
3.11	2.97	1.45	1.55
4.65	4.51	2.22	2.33
6.20	5.97	2.98	3.08
7.76	7.45	3.74	1.84
1.552	1.490	4.52	0.768
		5.27	
		0.761	

Zn: 1.521 ± 0.031

Fe: 0.764 ± 0.004

Zn/Fe = 1.521/0.764 = 1.99 ± 0.04

APPENDIX II- X-ray Diagrams

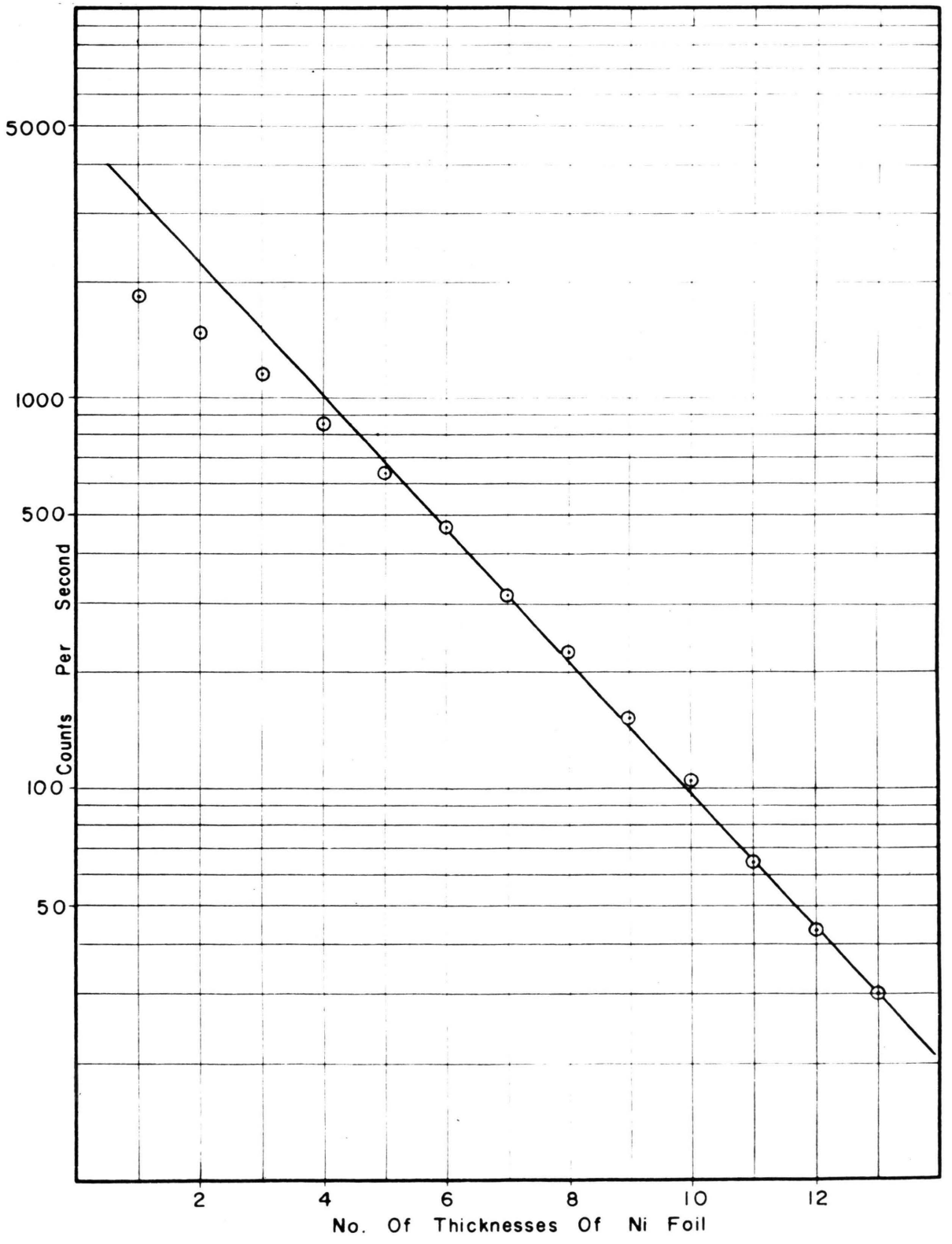


FIG. 7: LINEARITY OF THE GEIGER TUBE (Ni FOIL)

Fixed Time Operation — Input Signal - Neg. 40Kv
Scale Factor - 128 — Time Interval - 8 Sec. 18 ma.

APPENDIX II

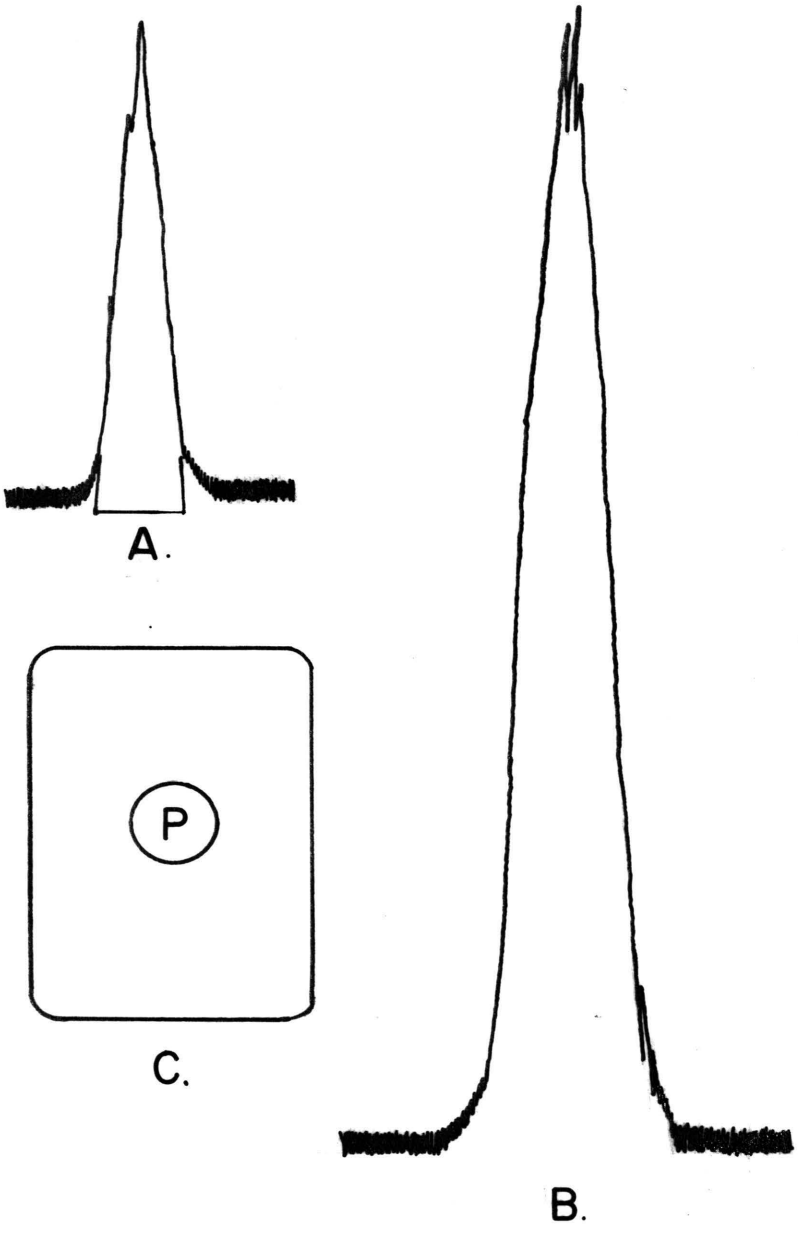


FIG. 8: SKETCH OF TYPICAL AND ATYPICAL FLUORESCENCE CURVES; SKETCH OF THE SAMPLE HOLDER

APPENDIX III - Results of 'wet' quantitative analysis

Sa.No.	Fe (ml)	Fe (mg)	Zinc Tit.	Zinc B.Tit.	Zn (mg)	Fe (avg)	Zn (avg)	Zn/Fe
4a	2.84	17.8	15.67	0.25	224.4	17.8	224.8	12.6
b	2.83	17.7	15.77	0.36	225.3			
9a	4.80	30.0	14.61	0.27	209.0	29.9	208.4	7.0
b	4.76	29.8	14.52	0.27	207.7			
11a	6.42	40.1	19.75	0.70	280.9	40.1	280.9	7.0
b	Ruined							
17a	2.92	18.2	17.08	0.21	244.9	18.6	246.0	13.2
b	3.10	19.4	17.31	0.55	247.1			
18a	3.80	23.8	17.39	0.46	248.06	23.6	247.4	10.5
b	3.72	23.3	17.28	0.43	246.73			
22a	3.04	19.0	16.97	0.10	243.9	18.8	243.8	13.0
b	2.96	18.5	17.01	0.28	243.6			
24a	4.34	27.1	17.29	0.40	247.1	27.3	246.0	9.0
b	4.40	27.5	17.30	0.88	244.8			

The iron samples were diluted to 100 ml in a volumetric flask, and two 40 ml aliquot portions were removed for the 'a' and 'b' results. Thus to arrive at milligrams iron from iron equivalents in milliliters, multiply by (2.50 mg/ml x 2.5) 6.25. The zinc samples were diluted to 100 ml and two aliquot portions were removed for separate analyses. Thus column 6 of the table is determined from columns 4 and 5 by:

(2.5 aliquot portions)·(5.76 mg/ml) is 14.4 for the ferrocyanide titration

The zinc standard is equivalent to 5 mg/ml zinc. Thus for sample 4a:

15.67(14.4) - 0.25(5) = 224.4 mg Zinc

VITA

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BIBLIOGRAPHY

Bailey, S. W. (1949) "Liquid Inclusions in Granite Thermometry"; Jour Geol 57:304-307

Bateman, A. M. (1952) Economic Mineral Deposits; John Wiley & Sons; 2nd Ed.; p. 36-44.

Bowen, N. L. (1928) "Geologic Thermometry"; Laboratory Investigations of Ores; McGraw-Hill; Chapt. 10

Brown, J. S. (1936a) "Structure and Primary Mineralization of the Zinc Mine at Balmat, N. Y."; Econ Geol 31:233-258

Brown, J. S. (1936b) "Supergene Sphalerite, Galena, And Willemite at Balmat"; Econ Geol; 31:331-354

Brown, J. S. (1947) "Porosity And Ore Deposition At Edwards and Balmat"; G S A; 58:505-546

Edwards, A. B. (1954) Textures Of The Ore Minerals; Aust. Inst. of Min. and Met.; esp. p. 83,84

Ermakov, N. P. (1944) "Determination of Temperatures of Formation of Hydrothermal Minerals By Studying Liquid Inclusions"; Comp. Rend. Acad. Sci. URSS; 45:202-204

Goldschmidt, V. M. (1954) Geochemistry; Oxford; p. 261-267

Ingerson, Earl (1947) "Liquid Inclusions In Geologic Thermometry"; Am Miner.; 32:375-388

Ingerson, Earl (1955) "Methods and Problems Of Geologic Thermometry"; Econ Geol; 50th Ann. Vol.:341-410

Kennedy, G. C. (1950) "Pneumatolysis And The Liquid Inclusion Method Of Geologic Thermometry"; Econ Geol; 45:533-547

Klug and Alexander (1954) X-Ray Diffraction Procedures; John Wiley & Sons

Kullerud, Gunnar (1953) "The FeS-ZnS System: A Geological Thermometer"; Norsk geol. tid.; 32:61-147

Laves and Goldsmith (1954) "On The Use of Calcic Plagioclases In Geologic Thermometry"; Jour Geol 62:405-411

Lindgren, Waldemar (1933) Mineral Deposits; 4th Ed.; McGraw-Hill Co.

Lowenstam and Epstein (1954) "Paleotemperatures Of The Post-Aptian Cretaceous As Determined By The Oxygen Isotope Method"; Jour Geol; 62:207-248

BIBLIOGRAPHY (Continued)

Newhouse, W. H. (1932) "The Composition of Vein Solutions As Shown By Liquid Inclusions In Minerals"; Econ Geol;27: 421-422

Newhouse, W. H. (1933) "The Temperature Of Formation Of The Mississippi Valley Lead-Zinc Deposits"; Econ Geol; 28:744-750

Peach, P. A. (1951) "Geothermometry Of Some Pegmatite Minerals Of Hybia, Ontario"; Jour Geol; 59:32-38

Scott, H. S. (1948) "Decrepitation Method Applied To Minerals With Fluid Inclusions"; Econ Geol; 43:637-654

Smith, F. G. (1947) "The Pyrite Geo-thermometer"; Econ Geol; 42:515-523

Sorby, H. C. (1858) "On The Microscopical Structure Of Crystals, Inciating The Origin of Minerals And Rocks"; Quat. Jour. Geol. Soc. London; 14:453-500

Stroiber, R. E. (1940) "Minor Elements In Sphalerite"; Econ Geol; 35:501-519

Twenhofel, W. S. (1947) "The Temperature of Crystallization Of A Fluorite Crystal From Luna County, New Mexico"; Econ Geol; 42:78-82

Winchell & Winchell (1951) Elements Of Optical Mineralogy; John Wiley & Sons